

# Optimal values of rovibronic energy levels for triplet electronic states of molecular deuterium

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Optimal set of 1050 rovibronic energy levels for 35 triplet electronic states of  $D_2$  has been obtained by means of a statistical analysis of all available wavenumbers of triplet-triplet rovibronic transitions studied in emission, absorption, laser and anti-crossing spectroscopic experiments of various authors. We used a new method of the analysis (Lavrov, Ryazanov, JETP Letters, 2005), which does not need any *a priori* assumptions concerning the molecular structure being based on only two fundamental principles: Rydberg-Ritz and maximum likelihood. The method provides the opportunity to obtain the RMS estimates for uncertainties of the experimental wavenumbers independent from those presented in original papers. 234 from 3822 published wavenumber values were found to be spurious, while the remaining set of the data may be divided into 20 subsets (samples) of uniformly precise data having close to normal distributions of random errors within the samples. New experimental wavenumber values of 125 questionable lines were obtained in the present work. Optimal values of the rovibronic levels were obtained from the experimental data set consisting of 3713 wavenumber values (3588 old and 125 new). The unknown shift between levels of ortho- and para- deuterium was found by least squares analysis of the  $a^3\Sigma_g^+$ ,  $v = 0$ ,  $N = 0 \div 18$  rovibronic levels with odd and even values of  $N$ . All the energy levels were obtained relative to the lowest vibro-rotational level ( $v = 0$ ,  $N = 0$ ) of the  $a^3\Sigma_g^+$  electronic state, and presented in tabular form together with the standard deviations of the empirical determination. New energy level values differ significantly from those available in literature.

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## I. INTRODUCTION

The present work is devoted to the studies of the wavenumbers of the triplet-triplet radiative electronic-vibro-rotational (rovibronic) transitions and empirical determination of the optimal set of the triplet rovibronic energy levels of the  $D_2$  molecule.

Studies of spectra and structure of molecular deuterium represent not only understandable general interest (an isotopomer of simplest neutral diatomic molecule), but have also direct practical value in connection with wide use of  $D_2$  in physical experiments and in various technical applications: from gas-discharge sources of ultraviolet radiation [1] up to tokamak-reactors [2].

The spectrum of the  $D_2$  molecule is caused by both singlet-singlet and triplet-triplet rovibronic transitions. The intercombination lines were not observed yet. The most interesting resonance singlet band systems are located in vacuum ultraviolet (VUV), while the triplet transitions are responsible for major part of light emission of ionized gases and plasma in near infrared, visible and near ultraviolet. They are often used for spectroscopic diagnostics of non-equilibrium plasmas [1, 2, 3, 4, 5, 6]. Therefore, the triplet rovibronic levels and optical transitions between them were chosen as the object of the present research.

The energy level values evaluated from experimental wavenumbers are often called *observed* energy levels irrespective of a method used for the data processing. Such rather disputable terminology implicitly assumes that all spurious experimental results and systematic errors are absent, and random errors are negligibly small (Otherwise, several different sets of the observed energy level values may be obtained from the same set of experimental wavenumbers by applying different methods of the data processing.). Therefore, we prefer to use the term *empirical* level values <sup>1</sup> (for any values obtained from experimental data) and *optimal* level values (for the values obtained by pure statistical approach [8, 9]), leaving the word *observed* for experimental values of the wavenumbers which are unambiguously linked with the wavelengths — real observables in spectroscopy. (It should be also mentioned that in molecular spectroscopy energy levels in  $\text{cm}^{-1}$  are often called molecular terms (see e.g. [10]). Absolute values of both levels and terms are always positive and calculated relative to the lowest vibro-rotational level of the ground electronic state considered as a

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<sup>1</sup> Compare with the term *experimental* level values in [7]

zero level. That is in contrast to original meanings of terms and energies adopted in atomic spectroscopy.)

Generally speaking, the best set of empirical values of energy may be named a set of optimum values (optimal for available experimental data) only if these values do not depend on a procedure of their obtaining, and are entirely defined only by amount and quality of available experimental data. In such favourable case the energy level values may be considered as secondary experimental data.

It is well known that diatomic hydrogen, being the simplest neutral molecule, has a most sophisticated emission spectrum. The hydrogen band spectrum, caused by spontaneous emission due to rovibronic transitions, does not show a visible, easily recognizable band structure, but has the appearance of a multiline atomic spectra. The peculiarity of molecular hydrogen and its isotopic species — abnormally small nuclear masses — leads to high values of vibrational and rotational constants and large separation between vibrational and rotational levels of various excited electronic states. As a result, various rovibronic spectral lines belonging to different branches, bands and band systems are located in the same spectral regions, leading to the overlap of various band systems, bands and branches, as well as the mixing of rovibronic spectral lines having different origins. The small nuclear masses stimulate a breakdown of the Born-Oppenheimer approximation due to electronic-vibrational and electronic-rotational perturbations having both regular and irregular character; this combination seriously complicates the interpretation of the spectra of hydrogen isotopomers and the unambiguous identification of rovibronic spectral lines. Symmetry rules for permutation of identical nuclei in homonuclear isotopomers ( $H_2$ ,  $D_2$  and  $T_2$ ) cause the known effect of the intensity alternation of neighbouring lines within the rotational structure of bands due to the alternation in degeneracy of successive rotational levels with odd and even values of rotational quantum number (e.g. 1:2 in the case of  $D_2$ ). This effect also masks the visible structure of branches resulting in serious additional difficulties for identification of rovibronic spectral lines.

Thus, most of the lines in the optical spectra of hydrogen isotopomers have not yet been assigned in spite of tremendous efforts by spectroscopists over the previous century [11, 12, 13, 14, 15, 16, 17]. As an example, in the latest compilation of experimental data for molecular deuterium  $D_2$  [16], the working list of 27488 recorded lines contains only 8243 assignments. These assignments were obtained by traditional methods of analysis using

wavenumber combination differences (method of common differences) and Dunham series expansions [11, 13], sometimes together with comparison of molecular constants obtained for different isotopic species [12]. Later on, the traditional methods were supplemented by taking into account the line intensities [18] and the results of *ab initio* and semi-empiric calculations [16, 17].

Recently in [19, 20], the identification of rovibronic lines of three singlet VUV band systems of  $D_2$  has been obtained by common use of semi-empiric calculations (of the levels and the transition probabilities) together with the program IDEN [21, 22] developed for visual identification of complex atomic spectra. Although the approach seems to be a rather powerful and prospective tool for finding new assignments in the spectra of hydrogen isotopomers, the final results of [19, 20] can not be considered as optimal values of the rovibronic energy levels for the  $D^1\Pi_u$ ,  $D^1\Pi_u$ , and  $B^1\Sigma_u$  electronic states studied in [19, 20]. They were simply calculated as the average of values derived from different observed line wavenumbers added to the corresponding lower vibro-rotational levels of the  $X^1\Sigma_g^+$  ground electronic state from [14], assumed to be known with negligible uncertainty. Actually, those lower levels were obtained from wavelengths of two other VUV band systems ( $B^1\Sigma_u^+ - X^1\Sigma_g^+$ ,  $C^1\Pi_u^- - X^1\Sigma_g^+$ ) by two independent methods of the analysis which gave noticeably different results (compare columns 2 and 4 of table 4 from [14]). It is evident that common use of experimental data for five singlet band systems mentioned above may give another set of rovibronic levels for  $X^1\Sigma_g^+$  ground electronic state. Then the level values for the excited states will be changed somehow. In our opinion, the assignments found in [19, 20] also should be confirmed by the appropriate statistical analysis of all available in literature experimental data on the wavenumbers for all other singlet band systems of  $D_2$ . For that purpose it is possible to use the approach proposed and realized in our papers [8, 9, 23, 24].

Currently, available information concerning triplet rovibronic energy level values of  $D_2$  molecule exists in the form of the list of molecular constants for Dunham series expansions in [15, 25], and tables of rovibronic levels obtained in [16].

In the case of the hydrogen molecule the Dunham coefficients are known to provide a very poor description of the rovibronic energy level values [26]. Moreover any set of molecular constants depends not only on molecular properties but also on the theoretical model used in the analysis of the spectrum (the type and length of the series expansion, form of a model Hamiltonian, etc.), as well as on amount of measured wavenumbers and even

on the distribution of the spectral lines over the vibrational and rotational levels (see e.g. [8, 9, 26, 27]). Therefore, the molecular constants are rather conditional and the procedures used for their determination are subjective in character. In practical use of reference data on molecular constants, the question arises as to how many rovibronic levels of a particular type can be described by a given set of constants with a required accuracy. In the best case, this question can be answered only by the researcher who obtained the given set of molecular constants. However, series expansions and molecular constants may be useful both in a process of classifying rovibronic lines in unknown spectra and in calculations which do not pretend for a high accuracy.

The data reported in [16], in general, give a rather good description of the  $D_2$  spectrum, but they are also not free from criticism. The method of the analysis used in [16] is based on the common use of the combination differences, some selected wavenumbers for certain transitions and one by one multistage treating of separate branches, bands and band systems. The sequence of the steps chosen in [16] is not the only possible analytical arrangement. Therefore, the data thus obtained can not be considered as an optimal set of levels providing the best description of all observed wavenumber values. On our opinion the reported in [16] uncertainty  $\sigma = 0.05 \text{ cm}^{-1}$  for all levels and all wavenumbers of lines is the overestimation caused by the randomization of various deviations when working with many thousands of levels and lines. It should also be mentioned that after publication of [16], new experimental data on the wavenumbers appeared [28, 29].

Recently, a new method of a pure statistical analysis of experimental data on the rovibronic transition wavenumbers for empirical determination of the optimal energy-level values has been proposed [8] and successfully applied for the derivation of rovibronic level values of the singlet states of the  $BH$  [23] and the triplet states of the  $H_2$  [24] molecules. The method is based on only two fundamental principles: Rydberg-Ritz and maximum likelihood. This approach differs from known techniques in several aspects: 1) does not need any assumptions concerning an internal structure of a molecule; 2) does not employ intermediate parameters, such as molecular constants in the traditional methods; 3) a one-stage optimization procedure can be used for all available experimental data obtained for various band systems, by various methods and authors, and in various works (Simultaneous adjustment of all levels eliminates the possibility of accumulative errors in traditional methods, caused by multi-step treating of various bands one by one, as well as by transfer of any occasional error for one

level, appeared on one step, for all higher levels obtained during further steps); 4) provides the opportunity of a rational censoring of the experimental data in an interactive mode (thus allowing the user the option to eliminate obvious errors (outliers) and misprints, to revise incorrect line assignments, and to compare various sets of experimental data for mutual consistency); 5) gives an opportunity of independent estimation of experimental uncertainties by analyzing the shapes of error distributions within various samples of the experimental data (It means that our statistical estimates of the root-mean-square (RMS) experimental errors are totally independent on the estimates reported in original experimental papers); 6) provides an optimal set of rovibronic level values as well as the uncertainties of their determination (standard deviations SD and the covariance matrix) caused only by the amount and quality of existing experimental data [9].

A necessary precondition for an application of the method [8] is an existence of more or less dependable assignments for majority of rovibronic spectral lines under the study. Therefore, the new method should be considered as complimentary for the traditional and new methods of identifying unknown spectra. However, since the new, pure statistical method is objective, it is better to consider any identification of a rovibronic spectrum as preliminary until it is not corroborated by that, the use of certain assignments in the framework of this method does not lead to contradictions with the Rydberg-Ritz principle or with normal distribution of random experimental errors.

The goal of the present paper is to report the results of applying the new method [8] for statistical analysis of the rovibronic spectral line wavenumbers of triplet band systems and determining the optimal set of rovibronic energy levels for all known 35 triplet electronic states of molecular deuterium:  $a^3\Sigma_g^+$ ,  $c^3\Pi_u^+$ ,  $c^3\Pi_u^-$ ,  $d^3\Pi_u^+$ ,  $d^3\Pi_u^-$ ,  $e^3\Sigma_u^+$ ,  $f^3\Sigma_u^+$ ,  $g^3\Sigma_g^+$ ,  $h^3\Sigma_u^+$ ,  $i^3\Pi_g^+$ ,  $i^3\Pi_g^-$ ,  $j^3\Delta_g^+$ ,  $j^3\Delta_g^-$ ,  $k^3\Pi_u^+$ ,  $k^3\Pi_u^-$ ,  $n^3\Pi_u^+$ ,  $n^3\Pi_u^-$ ,  $p^3\Sigma_g^+$ ,  $q^3\Sigma_g^+$ ,  $r^3\Pi_g^+$ ,  $r^3\Pi_g^-$ ,  $s^3\Delta_g^+$ ,  $s^3\Delta_g^-$ ,  $u^3\Pi_u^+$ ,  $u^3\Pi_u^-$ ,  $(7p)^3\Pi_u^+$ ,  $(7p)^3\Pi_u^-$ ,  $(8p)^3\Pi_u^+$ ,  $(8p)^3\Pi_u^-$ ,  $(9p)^3\Pi_u^+$ ,  $(9p)^3\Pi_u^-$ ,  $(6d)^3\Sigma_g^+$ ,  $(7d)^3\Sigma_g^+$ ,  $(8d)^3\Sigma_g^+$  and  $(9d)^3\Sigma_g^+$ .

## II. STATISTICAL APPROACH TO EMPIRICAL DETERMINATION OF OPTIMAL VALUES OF THE ROVIBRONIC ENERGY LEVELS

In principle an analysis of experimental data on wavenumbers of spectral lines may be considered as consisting from two separate parts: 1) an identification (classification, assign-

ment) of spectral lines (an establishment of a correspondence between observed spectral lines and pairs of the initial and final levels responsible for occurrence of these lines in a spectrum), and 2) the determination of energy level values from measured wavenumbers (or some other magnitudes related to the levels, like molecular constants [26], or potential curves [30]). The aim of the first stage of an analysis is to find most likely identification and to prove correctness of the assignments. The goal of the second is to obtain the best possible values of the energy levels as well as the uncertainties of their empirical determination. In spite of the difference in objectives these two parts of an analysis are closely connected because quality of final results in both cases is determined by their ability to reproduce observed spectra. Therefore, quite often the parts are not distinguished in original papers.

The main part of the present work represents the second stage of the analysis of the triplet-triplet spectrum of  $D_2$  molecule, based on the results of the first stage reported in [16, 28, 29, 31, 32, 33, 34, 35].<sup>2</sup> Therefore in the further consideration it is supposed, that more or less reliable identification is already established for the majority of lines. Then not numerous cases of wrong assignments may be revealed as outliers and corrected during the statistical analysis (see below).

All spectroscopic methods of empirical determination of energy levels of atoms and molecules are based on the Rydberg-Ritz combination principle corresponding to the Bohr frequency rule in quantum mechanics. For rovibronic transitions of diatomic molecules between electronic states corresponding to Hund's case "b" for angular momenta coupling (negligible multiplet splitting) it may be written as:

$$\nu_{n''v''N''}^{n'v'N'} = E_{n'v'N'} - E_{n''v''N''}, \quad (1)$$

where  $n$  indicates an electronic state, and  $v$  — the vibrational quantum number. In case of diatomic hydrogen isotopomers the multiplet splitting and hyperfine structure of levels and lines are negligibly small and usually unresolved in experiments, therefore in the present work rotational levels are characterized by the quantum number  $N$  of the total angular momentum of a molecule excluding spins of electrons and nuclei. Upper and lower rovibronic levels are marked by single and double primes, respectively. The  $\nu_{n''v''N''}^{n'v'N'}$  is the wavenumber

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<sup>2</sup> In some cases discussed below, we have had to do the job of the first stage when it was necessary to change earlier assignments and to obtain new experimental values of the wavenumbers of some questionable lines.

(recalculated for vacuum conditions) of the  $n', v', N' - n'', v'', N''$  rovibronic transition, and  $E_{nvN}$  are corresponding energy level values.

One may see that the experimentally measured wavenumbers of the spectral lines are related only to the differences between pairs of rovibronic energy levels. So the values of the levels cannot be directly obtained by means of the Rydberg-Ritz principle only. Therefore, traditional methods of empirical determining the rovibronic energy levels require the introduction of some additional (with respect to the Rydberg-Ritz combination principle) assumptions regarding properties of molecules and, hence, are semiempirical and allow some subjectivity of a researcher (see details in [9]).

The classification of the levels and lines by certain sets of quantum numbers ( $n, v, N$ ) is important for the assignment of the wavenumbers to the rovibronic levels between which the transitions occur and, in particular, for the application of the selection rules. When this assignment is carried out, the specific designations of the levels and lines are not important any more. The rovibronic levels may be denoted by natural numbers in an arbitrary order. The notation  $E_{nvN}$  may be changed to a more compact notation  $E_i$ , and the wavenumbers are designated by pairs of indices corresponding to the initial and final levels. Then the expression (1) becomes:

$$\nu_{ij} = E_i - E_j. \quad (2)$$

Suppose that the set of available experimental data consists of  $n_\nu$  wavenumber values obtained for  $n_T$  transitions caused by the combinations of  $n_E$  energy levels.  $n_\nu > n_T > n_E$  because an amount of the transitions allowed by selection rules usually considerably exceeds quantity of combining levels. Furthermore, experimental data for the same transitions may be obtained and reported in various publications. One may insert all experimental wavenumbers into left hand side of the (1) one by one, and consider the energy levels as adjustable parameters to be obtained from the experimental data. Then (1) turns into a system of  $n_\nu$  equations with  $n_E$  unknown quantities  $E_i$ . This system of equations is overdetermined and, hence, is inconsistent because the experimental data always involve measurement errors.

Straightforward general solution for solving such problems is well-known in mathematical statistics. That is the least squares method based on the assumption of finite second moment of the distribution function for random errors [36]. In our case it consists in the minimization of the weighted mean-square deviation between observed  $\nu_{ij}^{expt}$  and calculated (as differences



of adjustable energy levels  $E_i, E_j$ ) values of rovibronic line wavenumbers, or the sum

$$r^2 = \sum_{\nu_{ij}} \left[ \frac{(E_i - E_j) - \nu_{ij}^{expt}}{\sigma_{\nu_{ij}^{expt}}} \right]^2. \quad (3)$$

The values  $\sigma_{\nu_{ij}^{expt}}$  are the RMS estimates of experimental errors (one standard deviation — SD) for each experimental datum, and the summation is performed over all available experimental data. Due to the linearity of the equations (2), the optimization problem comes to solving a system of linear algebraic equations. The complete solution involves the inversion of the  $n_E * n_E$  sparse matrices. When the number of desired levels  $n_E$  is of the order of a thousand, as is usually the case, this problem can be solved even using modern personal computers. (see [9] for details)). If the experimental errors are random and distributed according to a normal (Gaussian) law, the obtained solution corresponds to the maximum likelihood principle [36].

The attempts to apply such statistical approach for determination of the energy level values appeared almost simultaneously in atomic (e. g. the spectra of the Er I, Er II [37], Cl II [38] by the inversion method, and the spectra of the Si I [39], Cl I [40] by the iterative method) and in molecular [14, 41] spectroscopy when first digital computers became available. It is interesting to note, that in spite of obvious disadvantages of the iterative method (the problems of convergence and lack of the covariance matrix (see p.6 in [42])), its usage can be met in current publications (see e.g. [43]).

In several studies reviewed by Åslund in [41], it was proposed to determine the rovibronic levels of molecules on the basis of the combination principle by solving the overdetermined system of equations with the use of a computer. Owing to the limited capabilities of the computers of the day, the optimization procedure was realized for processing the wavenumbers for separate bands only. As a result, those authors overlooked the opportunity to overcome the problem of the limitations for the method of common differences caused by the Laporte's selection rule allowing rovibronic transitions only between levels with different + and - parities [8]. (Only recently, it was shown that, if it is possible to use experimental data on rovibronic lines that pairwise couple *three or more* different electronic-vibrational states, then the system of equations (1) contains the link between the line wavenumbers and the values of all rovibronic levels involved [8]. Thus, in the case of heteronuclear molecules the above problem of the existence of uncoupled sets of the levels with even and odd rota-

tional quantum numbers disappears.) Consequently, the relative positions of unrelated odd and even rotational levels, as in traditional approaches, were obtained using the Dunham approximation and molecular constants. It should be noted that the attempts of direct empirical determining the rovibronic levels in [41] were inconsistent from the very outset. The level values were considered as some intermediate parameters of a molecule, and the procedure of their determination was only one of the steps on the long way from the measurement of the line positions on a photographic plate up to obtaining a particular set of vibrational-rotational constants for various electronic states. Later on, Åslund [44] actually abandoned his initial idea in favour of so-called *direct approach* [27] based on the one-step optimization of sets of vibro-rotational constants for upper and lower electronic states of a bad system.

The empirical determination of the energy level values by means of the least squares method looks natural and simple, but its correct realization in practice encounters serious difficulties. The matter is that the result of the minimization of (3) (i. e. the optimal set of the level values and the matrix of co-variances) depends not only on the values of experimental data, but also on weighting of various data (i. e. from what values of the error estimates  $\sigma_{\nu_{ij}^{expt}}$  are included into the input data set). Therefore, for the correct optimization of the adjusted parameters (required level values) it is necessary to know a dependable RMS error estimate for each experimental wavenumber value, or to have the set of the wavenumbers consisting from several subsets (statistical samples) of uniformly precise data with known RMS error estimates for each sample.

Unfortunately, authors of experimental works usually limit themselves to some remarks of general character (concerning resolving power of a spectrograph, linear dispersion, typical line widths, *etc.*) and, at the best, to some rough estimates of an order of magnitude or the upper limit of possible experimental uncertainty. Most often the real accuracy of the reported data is uncertain. The situation in the literature containing experimental data analyzed in the present work will be illustrated below, but it should be mentioned that the same uncertainty may be met even in current publications. (To not be unsubstantiated, very recent paper [43] may be used as a typical example. In the part describing experimental setup one may read: "The estimated error is +0.005 Å for single lines, but many lines are blended in complex emission peaks."; while in the part describing data processing one may find: "As input to the code, 1314 classified lines were used with uncertainties on their wave

numbers smoothly decreasing from 0.33 to 0.10  $\text{cm}^{-1}$  between 1150 and 2800  $\text{\AA}$ .” Attentive reader can easily recognize that the wavenumber uncertainties correspond to wavelength uncertainties 0.0044 and 0.0078  $\text{\AA}$  not equal to those for single lines. But a lot of questions remain. What about blended lines? Why the weighting of various data depends only on wavenumber values? What kind of the smooth decrease was chosen and why? We hope that the authors have certain answers and did their best to get best possible level values they are interested in. But what an independent researcher can be able to do with those wavenumbers after several decades?)

The problem of weighting various experimental data according to their accuracy in the framework of the least squares fitting was mentioned from the very beginning [37]. But in practical applications it was always considered as an issue of secondary importance, leaving a lot of room for author’s subjectivity. May be it is because researchers use to process their own experimental data and have certain opinions concerning their accuracy. Then, irrespective of the way of the data processing, the empirical level values are considered as optimal when they are able to reproduce experimental wavenumbers with an accuracy corresponding to author’s estimates for the experimental errors (“chosen tolerance”). That is certainly reasonable, but only if author’s expectations coincide with real experimental uncertainty caused by all possible sources of errors. Thus, in spite of principle objectivity of the least squares method the results of its application have subjective character reflecting author’s individuality. Achilles’ heel of all known to authors of the present work papers devoted to the determination of the level values by means of the least squares adjustment is ignoring or subjective estimating of the experimental errors.

Development of pure statistical approach to the problem of empirical determination of energy level values [8] was motivated by author’s desire to overcome the subjectivity discussed above. Main ideas of the approach may be formulated in the following way. Since optimal values of rovibronic levels are to be entirely defined only by amount and quality of available experimental data, a procedure of their obtaining should be based only on the fundamental principles. Rydberg-Ritz combination principle provides the link between experimental wavenumbers of rovibronic transitions and desired energy levels. Maximum likelihood principle gives the optimization criterion in the form (3) for the normal distribution function of random errors. The set of input data for minimizing (3) should be prepared by means of statistical analysis: 1) The data having systematic errors and spurious results

(outliers) should be uncovered and eliminated; 2) The whole set of available experimental data should be divided into finite number of subsets (samples) of uniformly precise data with normal error distributions; 3) the values of an experimental RMS uncertainty for the samples (unique for all data belonging to the same sample) are obtained, being independent from those named in original papers. Optimal set of the rovibronic level values is obtained from the prepared input data set in the one-stage optimization procedure. The accuracy of empirical determination of the optimal level values is characterized by the covariance matrix  $D(E)$ , square roots of its diagonal elements are used as the uncertainties (one SD) of the level values ( $\sigma_{E_i} = \sqrt{D_{ii}(E)}$ ). (The method may be easily generalized for other types of the distribution function of random errors.)

The computer code developed for practical realization of the method is based on the minimization of the weighted mean-square deviation (3) by the inversion of the  $n_E * n_E$  sparse matrices [8, 9]. The  $\nu_{ij}^{expt}$  and  $\sigma_{\nu_{ij}^{expt}}$  values are the input data, while the optimal set of the energy levels  $E_i$  and their covariance matrix  $D(E)$  are the output data of the minimization. The later is used for calculating and visualization of various quantities suitable for interactive statistical analysis of the experimental data including rational censoring of various groups (samples) of the data and the derivation of the RMS uncertainties of experimental data independent from those reported in original papers.

The interactive analysis consists in the studies of the shape of the distribution functions of the weighted unbiased deviations

$$\xi_{ij} = \frac{\nu_{ij}^{expt} - (\tilde{E}_i - \tilde{E}_j)}{\sigma_{\nu_k}}, \quad (4)$$

for various sets (statistical samples) of the experimental wavenumbers,  $k$  being the number of the sample. Here the  $\nu_{ij}^{expt}$  is certain experimental datum for the wavenumber of the  $i$  -  $j$  transition, while the level values  $\tilde{E}_i$  and  $\tilde{E}_j$  are obtained by the minimization of (3) without using the particular datum under the consideration. The  $\sigma_{\nu_k}$  is adjustable value of the estimate for experimental uncertainty (RMS error estimate) common for all the data included into the sample. The dimensionless deviation  $\xi_{ij}$  characterizes a degree of coordination of the particular experimental datum  $\nu_{ij}^{expt}$  with all other experimental data in the framework of the Rydberg-Ritz principle. Among all, the most important are certainly the data obtained for the same rovibronic transition in various works, and the wavenumbers of other lines directly connected with the upper  $n'$ ,  $v'$ ,  $N'$  or the lower  $n''$ ,  $v''$ ,  $N''$  rovibronic

levels.

The values  $\tilde{E}_i$  and  $\tilde{E}_j$  may be expressed through the corresponding level values and the covariance matrix  $D(E)$  obtained with the use of all experimental data, then

$$\xi_{ij} = \frac{\nu_{ij}^{expt} - (E_i - E_j)}{\sqrt{\sigma_{\nu k}^2 - (D_{ii}(E) + D_{jj}(E) - 2D_{ij}(E))}}, \quad (5)$$

where  $D_{ij}(E)$  are elements of the covariance matrix. This makes it possible to obviate the need for the repeated minimizing (3).

The empirical accumulative distribution function for each data sample is defined by

$$F(\xi) = \frac{1}{n_\nu} \sum_{\xi_{ij}} I(\xi_{ij} \leq \xi), \quad (6)$$

where  $n_\nu$  is the number of elements in the sample,  $I(A)$  — the indicator of event  $A$ .<sup>3</sup> Here the sum is over all data included into the sample. After each minimization of (3) it is possible to calculate and to see  $F(\xi)$  for any sample of the  $\xi_{ij}$  values chosen by the user of the computer code. That gives an opportunity to study various data samples selected from the complete set of all experimental data by some physical considerations: the data reported in the certain paper, wavenumbers of lines from the certain interval of wavelengths, or belonging to the certain band, or to the certain band system.

It is evident that if all the data  $\nu_{ij}^{expt}$  included into some sample are free from systematic errors and have normal distribution of random errors with RMS estimate equal to  $\sigma_{\nu k}$ , then the empirical distribution  $F(\xi)$  should be close to normal cumulative distribution function with the zero mean and variance equal to unity, namely

$$F_0(\xi) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\xi} \exp(-\frac{x^2}{2}) dx. \quad (7)$$

Therefore, it is useful and convenient to provide the interactive analysis of experimental wavenumber values by studies of the shape of the empirical functions

$$\Phi(\xi) = F_0^{-1}(F(\xi)), \quad (8)$$

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<sup>3</sup>  $I(\xi_{ij} \leq \xi) = 1$  for  $\xi_{ij} \leq \xi$  and  $I(\xi_{ij} \leq \xi) = 0$  for  $\xi_{ij} > \xi$ .

calculated for various groups (samples) of available data. Here  $F_0^{-1}$  is the function reverse to  $F_0(\xi)$ , i.e.  $F_0^{-1}(F_0(\xi)) \equiv \xi$ .

If the empirical distribution function  $F(\xi)$  is close to normal distribution, the empirical function (8) is close to linear function

$$\Phi(\xi) = \xi. \quad (9)$$

The way of dividing (sampling) the whole set of experimental data onto the subsets is not determined leaving some subjectivity for a researcher. But the shape of the function  $\Phi(\xi)$  is objective characteristic of the sample being determined by experimental values of the wavenumbers, Rydberg-Ritz principal and only one arbitrary parameter  $\sigma_{\nu k}$ . If for a certain data sample adjusting the value of the  $\sigma_{\nu k}$  leads to the shape of  $\Phi(\xi)$  fulfilling the criterion (9), the data included into the sample are to be considered as measured with uniform precision and characterized by the normal distribution of random experimental errors. The obtained value  $\sigma_{\nu k}$  is their experimental uncertainty (RMS error estimate). Thus, the method of *a posteriori* statistical analysis proposed in [8, 9] gives the objective mean to get proper results by the studies of the  $\Phi(\xi)$  functions, trying various kinds of sampling and adopting or rejecting various guesses. First applications of the approach in our recent studies of rovibronic spectra of  $BH$  and  $H_2$  molecules [8, 9, 23, 24] showed that the method allows revealing and rejecting both single outliers (caused by wrong assignments, blending, spurious readings and misprints) and large data sets, including data of some experiments (probably caused by systematic error of the wavelengths calibration [9]).

### III. STATISTICAL ANALYSIS OF PUBLISHED WAVENUMBERS OF TRIPLET ROVIBRONIC TRANSITIONS

All available values of rovibronic transition wavenumbers studied in emission, absorption, laser and anticrossing spectroscopic experiments of various authors [16, 28, 29, 31, 32, 33, 34, 35] were analyzed in the present work. In overwhelming majority of the works the fine and hyperfine structures of lines have not been resolved, and the reported experimental wavenumbers correspond to intensity maxima of the observable line profiles. In cases of partly resolved structure of lines [28, 29] we used wavenumbers of the brightest components.

The all identified triplet electronic transitions are naturally divided into three groups of

the band systems. These are: i) the 9 band systems having one common low electronic state ( $n^3\Lambda_g - a^3\Sigma_g^+$ , with  $\Lambda = 0, 1$  and  $n = 3 - 9$ ); ii) the 12 band systems having another common low state ( $n^3\Lambda_u - c^3\Pi_u$ , with  $\Lambda = 0 - 2$  and  $n = 3 - 9$ ); and iii) the 7 band systems connecting various  $n^3\Lambda_g$  and  $n^3\Lambda_u$  electronic states (with  $\Lambda = 0 - 2$  and  $n = 2 - 4$ ) including the  $a^3\Sigma_g^+ - c^3\Pi_u$  transitions. Therefore, the whole set of available experimental data possesses different informational content about rovibronic levels of different electronic states. Thus, the information on rovibronic levels of the  $c^3\Pi_u$  electronic state is contained in the wavenumber values of the 13 band systems, about the  $a^3\Sigma_g^+$  state — 10 band systems, and about for example the  $e^3\Sigma_u^+$  state — 6 band systems. For some electronic states as a source of the information about rovibronic levels we can use wavenumbers of lines from very few or even only one band system. In such cases the obtained values of the rovibronic levels are essentially less reliable.

Most of the data used in our statistical analysis are those collected from earlier works (partly unpublished) and reported in [16]. This compilation contains wavenumbers of 3117 rovibronic spectral lines assigned as triplet-to-triplet transitions. 31 from them have unassigned upper electronic and vibrational states. They were not used in the analysis, so only 3086 experimental data were taken from [16]. The 83 wavenumber values obtained in [33] coincide with those reported in [16] (although 12 of them appeared in Appendix C of [16] as unassigned). To prevent doubling of the same experimental results we excluded 71 wavenumbers from the data sets of [33]. The data reported in [31, 32] and [16] are obtained for the lines of the same band systems, but wavenumber values are different. Taking into account random character of the differences we decided to consider the data of those papers as the results of independent experiments. Thus, the initial data set used for the start of the statistical analysis contains: 350 wavenumbers from paper [32], 285 from [31], all 37 data from [34], 12 from [33], 1 from [35], 3086 from [16], 81 from [28], and 3 from [29]. It should be stressed that the wavenumbers of spectral lines used in the present work are spread over the very wide range 0.896—28166.84 cm<sup>-1</sup> from radio frequencies up to the ultraviolet.

On the first iteration of our statistical analysis we assumed, that all sets of experimental data presented in various papers represent the samples of uniformly precise data with RMS error uncertainty equal to the estimates presented in original experimental works. In the review [16] there are two remarks concerning accuracy of the wavenumbers. In experimental part it is written: "... the widths of the lines themselves limited the attainable accuracy,

which was a few hundreds of a  $\text{cm}^{-1}$ . At the end of the analysis the authors of [16] mentioned: "The mean (O-C) value for all triplets is  $-0.001 \pm 0.051 \text{ cm}^{-1}$ ", and came to the conclusion that "The precision of the measurements appear to be roughly uniform from the infrared to the ultraviolet". In spite of doubtfulness of such estimations we have accepted the value  $\sigma_\nu = 0.05 \text{ cm}^{-1}$  in the first iteration of our analysis for all wavenumbers taken from [16]. In papers [31, 32, 34] experimental errors are not mentioned at all. Therefore, we used the same value  $0.05 \text{ cm}^{-1}$  taking into account the estimates made by the same scientific group. In [33] it is written: "... the errors in the wave number of good lines should not exceed a few times  $0.01 \text{ cm}^{-1}$ ". We certainly don't know which lines are good or bad, therefore in this case we again took  $\sigma_\nu = 0.05 \text{ cm}^{-1}$ . For the data taken from [28, 29, 35] we used author's estimates  $\sigma_\nu = 0.01, 0.003, 0.0003 \text{ cm}^{-1}$ , respectively. Under these assumptions we obtained a set of energy levels by minimization of (3) and the empirical function  $\Phi(\xi)$  shown in figure 1.

One may see that the distribution function  $F(\xi)$  is far from the normal distribution  $F_0(\xi)$  ( $\Phi(\xi)$  is too far from the dotted straight line representing the case of normal distribution). Too many experimental wavenumber values significantly exceed those calculated as differences of corresponding energy level values. The distribution is not close to normal even in the area of small deviations ( $\xi < 3$ ). We suppose that this disagreement is caused by the deviations of real experimental wavenumber errors and their estimates, reported in original works. (On this stage of our analysis it was observed that 33 lines with wavenumbers measured in [16] are the combinations of 55 rovibronic levels representing the blocks of levels totally disconnected with all other triplet rovibronic levels of  $D_2$ . Therefore this wavenumbers were excluded from further consideration as useless. Therefore, only 3053 from the data reported in [16] are useful for further analysis.)

Thus there is the necessity of independent estimating of experimental uncertainties of the measured wavenumbers. To carry out this estimation we need to divide the data set used in the first iteration into some groups (subsets, samples) so, that all experimental data inside one subset can be considered as uniformly precise. We tried to sort experimental data to subsets taking into account various criteria, selecting the data obtained in various papers, in various wavelength regions and in various band systems. But acceptable results for error estimates were obtained only when we considered each band as a group of uniformly precise data. May be that way of sampling is fruitful because the lines of each band are located



in narrow parts of the spectrum, and different bands are usually measured and treated by different people even within the same scientific group. It should be also mentioned, that such approach gave reasonable results in similar analysis of  $BH$  [23] and  $H_2$  [24] spectra.

Each  $m$ -th iteration consists of: 1) the minimization of (3) with certain  $m$ -th set of the input data prepared at the last stage of the previous  $(m-1)$ -th iteration. It includes certain amount of experimental wavenumbers divided into finite number of samples characterized by certain RMS estimates for experimental errors in each  $k$ -th sample  $\sigma_{\nu k}^{(m-1)}$ ; 2) the output data (optimal energy levels  $E_i^{(m)}$  and the covariance matrix  $D_{ij}^{(m)}$ ) are used for calculating the  $\Phi^{(m)}(\xi)$  functions for each sample. That gives us an opportunity to analyze the shapes of the  $F_k^{(m)}(\xi)$  distribution function for all the samples and to find outliers. The data with  $\xi_{ij}^{(m)}$  larger than 3 were qualified as outliers. In all cases this criterion of censoring was less strong then commonly adopted Chauvenet's and Peirce's criterions [45]; 3) The new set of input data for the next  $(m+1)$ -th iteration is prepared by excluding the outliers from current  $(m)$ -th data set, and by obtaining for each sample new values of RMS estimates for experimental errors  $\sigma_{\nu k}^{(m)}$  by multiplying the  $\sigma_{\nu k}^{(m-1)}$  by the factor which should move the  $\sigma_{\xi k}$  closer to unity on the next iteration. Usually we used the expression  $\sigma_{\nu k}^{(m)} = \sigma_{\nu k}^{(m-1)} \sigma_{\xi k}^{(m)}$ , which is not strict due to the nonlinear link between  $\sigma_{\nu k}^{(m)}$  and  $\sigma_{\xi k}^{(m+1)}$ .

The square roots of the second moments  $\sigma_{\xi k}^{(m)}$  for empirical distribution functions  $F_k^{(m)}(\xi)$  (for each sample in each iteration) are calculated as

$$\sigma_{\xi k}^{(m)} = \sqrt{\sum_{\xi_{ij}^{(m)}} (\xi_{ij}^{(m)} - \langle \xi_{ij}^{(m)} \rangle)^2 F_k^{(m)}(\xi_{ij}^{(m)})}, \quad (10)$$

where  $\langle \xi_{ij}^{(m)} \rangle = \sum_{\xi_{ij}^{(m)}} \xi_{ij}^{(m)} F_k^{(m)}(\xi_{ij}^{(m)})$ , and the summing is performed over all the data included into the  $k$ -th sample.

The method of independent error estimation of wavenumbers belonging to the same  $k$ -th sample may be illustrated by considering one typical example — analysis of the  $(0-1)$  band of the  $e^3\Sigma_u^+ - a^3\Sigma_g^+$  electronic transition. 30 spectral line wavenumber values for  $R$ - and  $P$ -branch lines from this band are reported in [16]. The lines  $R18$  and  $R19$  are caused by the transitions between the  $(E_{e,0,19}, E_{a,1,18})$  and  $(E_{e,0,20}, E_{a,1,19})$  pairs of rovibronic levels, respectively. Mutual positions of these levels can be derived using wavenumber values of these lines only, because there are no other lines, which provide information about these levels. Then the value (4) for these lines is equal to zero. We don't take into account such

lines when calculating empirical distribution functions  $\Phi_k^{(m)}(\xi)$ .

The empirical function  $\Phi_k^{(1)}(\xi)$  obtained during first iteration (based on the sample of remaining 28 experimental wavenumbers characterized by common estimate  $\sigma_{\nu k}^{(0)} = 0.05 \text{ cm}^{-1}$  mentioned in [16]) is presented in figure 2(a). One may see, that the distribution  $F_k^{(1)}(\xi)$  is far from the normal distribution, which is represented by a dotted line on the figure. The square root of the second moment of this distribution  $\sigma_{\xi k}^{(1)} = 0.56 \pm 0.14 = 0.56(14)$  is not close to unity. We may try to shift the  $\sigma_{\xi k}^{(2)}$  to unity by changing error estimation in the following way:  $\sigma_{\nu k}^{(1)} = \sigma_{\nu k}^{(0)} \sigma_{\xi k}^{(1)} = 0.028(8) \text{ cm}^{-1}$ .

In the second iteration for the band under the consideration we used the same set of experimental data but new value of  $\sigma_{\nu k}^{(1)}$  instead of  $\sigma_{\nu k}^{(0)}$ . The empirical function  $\Phi_k^{(2)}$  is shown in figure 2(b). One may see that now the majority of lines shows the deviations sufficiently closer to the normal distribution, and the square root of the second moment  $\sigma_{\xi k}^{(2)} = 0.9(3)$  is closer to unity. But one point located in the bottom left corner of the figure is in contradiction with rest of the distribution. This point represents the  $\xi$  value for the line  $P10$ . The measured wavenumber value of this line  $\nu_{a,1,10}^{e,0,9} = 9292.16 \text{ cm}^{-1}$  deviates from the difference of corresponding energy level values derived in this iteration  $\nu_{a,1,10}^{e,0,9} - (E_{e,0,9}^{(2)} - E_{a,1,10}^{(2)}) = -0.0950 \text{ cm}^{-1}$ . The deviation exceeds our estimate for RMS error  $\sigma_{\nu k}^{(1)} = 0.028(8) \text{ cm}^{-1}$  more than three times. Thus the experimental wavenumber for the  $P10$  line should be excluded from the input data set as the outlier.

In the third iteration we used 27 wavenumber values and common uncertainty  $\sigma_{\nu k}^{(2)} = \sigma_{\nu k}^{(1)} = 0.028(8) \text{ cm}^{-1}$ . The function  $\Phi_k^{(3)}(\xi)$  thus obtained is shown in figure 2(c). One may see that this distribution function is not close to normal distribution function mainly because  $\sigma_{\xi k}^{(3)} = 0.60(8)$  is too far from unity. Therefore we have to correct the experimental uncertainty as  $\sigma_{\nu k}^{(3)} = \sigma_{\nu k}^{(2)} \sigma_{\xi k}^{(3)}$ . After certain number of iterations we are coming to  $\sigma_{\nu k} = 0.012(1) \text{ cm}^{-1}$ . Then on the next iteration we have empirical  $\Phi_k(\xi)$  function shown in figure 2(d) and the square root of the second moment  $\sigma_{\xi k} = 1.0(1)$ . One may see that now the experimental distribution function  $F_k(\xi)$  is close to the normal distribution function with zero mean and the variance equal to unity.

Thus, the sample of the 27 wavenumbers under the study may be considered as a group of uniformly precise experimental data with RMS estimate for random errors  $\sigma_{\nu k} = 0.012(1) \text{ cm}^{-1}$ . It should be underlined that our estimate is less than a quarter of the value  $0.05 \text{ cm}^{-1}$  declared in [16].

In that way we estimated RMS uncertainties of experimental data by the rational censoring of experimental data and determination of proper values of  $\sigma_{\nu k}$ .

After several dozens of iterations described above we came to the conclusion that 234 experimental data representing 228 spectral lines have to be excluded as outliers. Remaining 3588 wavenumbers were organized as 317 samples of uniformly precise data with RMS uncertainties obtained by the statistical analysis. RMS errors for many bands are so close that it seems reasonable to provide the enlargement of samples by merging studied samples having close values of RMS error. This also helps to improve statistics because some bands have small amount of data. It is reasonable to unite into the same sample wavenumbers of various bands with RMS errors getting to the certain wavenumber interval. The amount and widths of such intervals are uncertain. The choice of these parameters may lead to some subjectivity. On one hand, the widths of intervals should be large enough for the amount of data included in each interval be sufficient for statistics. But on the other hand, it should be as small as possible, not to disturb the close to normal error distributions obtained for separate bands. Our computational experiments show, that the intervals  $(0.00 \div 0.01) \text{ cm}^{-1}$ ,  $(0.01 \div 0.02) \text{ cm}^{-1}$ ,  $(0.02 \div 0.03) \text{ cm}^{-1}$ , etc. fulfil the requirements mentioned above. It is important, that all energy level values, obtained by the minimization of (3) with experimental data divided into the such enlarged samples of this size, have been changed significantly less than one SD of their determination with the original 317 samples.

After that, the whole set of the 3588 experimental data was reorganized into the 17 enlarged samples of uniformly precise data from [16, 28, 31, 32, 33, 34]. The RMS error estimates for each of these 17 subsets were derived by the method similar to described above. The results of the distribution of the data among the 17 samples together with the list of RMS error estimates for the wavenumbers of lines belonging to various vibronic bands is presented in table 1 of [46]. Also 1 wavenumber from [35] and 3 wavenumbers from [29] were used in further analysis as two separate samples (18-th and 19-th) with RMS errors reported in original papers, because the errors were unchanged during the analysis.

The amount of experimental data  $n_\nu$  in each of the new samples is presented in figure 3. It is seen, that the amount of data in each sample obtained by the enlargement is sufficient for carrying out the statistical analysis. Moreover, the distribution of data over the error steps looks quite plausible: the number of too precise data ( $\sigma_{\nu k} = (0.00 \div 0.01) \text{ cm}^{-1}$ ) is small ( $\approx 9\%$ ), most of the data ( $\approx 85\%$ ) are measured with realistic accuracy ( $0.01 \div 0.06$ )

$\text{cm}^{-1}$ , and the quantity of data monotonously falls down with further increase in the error estimate  $\sigma_{\nu k}$ .

Empirical functions  $\Phi(\xi)$  for first six united samples representing vast majority of useable experimental data are shown in figure 4. Correspondent values of RMS error estimates for each sample are shown in the figure. One may see that the error distribution functions are in much better accordance with normal distribution function then those obtained for the data samples representing separate bands (see figure 2).

Thus, splitting of experimental data into the samples and the subsequent enlargement of the samples as a whole were justified. Taking into account high enough statistics of the samples we are coming to the conclusion that obtained error estimates with a high probability are close to the values of the real experimental uncertainty.

#### IV. EXPERIMENTAL DETERMINATION OF WAVENUMBERS FOR QUESTIONABLE LINES

The statistical analysis of the 3822 known to authors published wavenumber values has shown that 3588 of them are useable for empirical determination of the level values, while the 234 experimental data (concerning 228 spectral lines) have to be excluded as outliers. 161 of those questionable lines are located within the wavelength range  $4300 \div 7300 \text{ \AA}$  available for us. 26 from them are the data reported in old [31, 32] papers and the wavenumber values for these lines were measured once more and corrected in the compilation [16]. For remaining 135 lines we decided to provide independent experimental determination of their wavenumbers. For that purpose we use the emission spectra of  $D_2$  obtained during our studies of translational and rotational temperatures in hydrogen and deuterium containing plasmas [3]. Detailed description of the experimental setup was reported elsewhere [47]. Capillary arc discharge lamps DDS-30 described in [48] have been used as a light source. They were filled with about 6 Torr of the spectroscopically pure  $D_2 + H_2$  (9:1) mixture. The range of the discharge current was from 50 to 300 mA (current densities  $j = 1.6 \div 10 \text{ A/cm}^2$ ). The light from the axis of plasma inside the capillary was directly focused by an achromatic lens on the entrance slit of the Czerny-Turner type 1 m double monochromator (Jobin Yvon, U1000). The intensity distribution in the focal plane of the spectrometer was recorded by cooled CCD matrix detector of the Optical Multichannel Analyser (Princeton

Appl. Res., OMA-Vision-CCD System).

For identification of the  $D_2$  spectral lines in our spectrum we used the assignments and wavelength values from [16]. Those values show certain spread around monotonic dependence of the wavenumber from the distance along the direction of dispersion in the focal plane of the spectrograph. The dispersion function of the spectrograph was obtained by the polynomial least squares fitting of the wavelengths versus the distance for strong unblended lines. Such wavelength calibration allow us to get new experimental values for the wavenumbers of 125 questionable spectral lines. The new values differs from those reported in [16] not only because of the smoothing procedure. In contrast to previous works we used digital intensity registration providing linear response of the CCD detector. That gave us the opportunity of digital deconvolution of the recorded spectra to resolve the major part of blended lines. The observed line profiles were determined mainly by Doppler and instrumental broadening. For strong unblended lines they were close to Gaussian shape except of insignificant far wings (see e. g. bottom graph in figure 5). Therefore, the parts of spectra in the neighbourhood of the blended questionable lines under the study were approximated by the superpositions of certain number of lines having Gaussian profiles with fixed half width and adjustable intensity and wavelength values. Then we obtained new values for the maximum intensities of  $D_2$  lines. Typical example is shown in the figure 5. One may see that the new values of the rovibronic transition wavenumbers are a little bit different from those reported in [16]. In our experimental conditions the intensities of 10 questionable lines were too weak for detecting and unambiguous separation by the deconvolution.

The uncertainty of our experimental data is mainly determined by errors of the deconvolution process. It should be underlined, that most of the questionable lines are blended lines of relatively low intensity. In that case it is not easy to obtain reliable RMS estimates for experimental errors. Therefore we used statistical method for derivation of experimental uncertainty described above. The new wavenumber values were included into the input data set obtained in the last stage of previous section as a separate (20-th) sample of uniformly precise experimental data. After several iterations the root mean square estimate of experimental uncertainty  $0.06 \text{ cm}^{-1}$  was obtained without any evidence for existence of outliers. The experimental  $\Phi(\xi)$  function for the sample of new wavenumbers for questionable lines is shown in Figure 6 together with corresponding frequency diagram. One may see that the distribution function of random errors is close to the normal distribution. Moreover

new wavenumber values do not contradict to the rest of the data set and may be used for determination of optimal values of rovibronic levels.

The new wavenumber values of questionable lines obtained in the present work are listed in table I together with those from [16]. One may see that in most cases the differences between new and old data are significant. Most often small differences ( $< 0.05 \text{ cm}^{-1}$ ) are probably caused by errors of reading from photographic plates and/or by round-up errors, when the vacuum wavenumbers were calculated from the wavelengths measured in air. In our case they were eliminated by digital reading of the intensity profiles and smoothing procedure of the determination of the dispersion curve. The differences higher than  $0.05 \text{ cm}^{-1}$  are caused by blending (by shifts of the intensity maxima or by disappearance of a weak line within the profile of the strong one, see e.g. figure 5), misprints and wrong assignments. The differences (O-C) between Observed wavenumber values and those Calculated as differences of corresponding optimal energy level values obtained in the present work are also shown in table I. One may see that in the framework of Rydberg-Ritz principle the new experimental data for 125 questionable lines are in much better co-ordination with the 3588 wavenumbers of other lines than those reported in [16].

## V. RESULTS AND DISCUSSION

Information on the amount of experimental data reported in original papers and the amount of outliers revealed by statistical analysis is presented in table II.

After all, the input data set consists of 3713 wavenumber values (3588 old and 125 new) divided into 20 subsets of uniformly precise data with known RMS estimates of experimental uncertainties obtained in the present work by pure statistical analysis, i.e. independent from the estimates reported in original papers. This data set was used for determination of optimal values of all studied experimentally triplet rovibronic levels by minimizing (3). The empirical function  $\Phi(\xi)$  thus obtained is presented in figure 7. One may see that the final distribution function  $F(\xi)$  is close to the normal distribution  $F_0(\xi)$ . Small deviations from the linear plot are caused by insufficient statistics for the data showing too high values of the weighted deviations  $|\xi_{ij}|$  (without any contradiction with the Chauvenet's criterion). Thus, optimal values of the 1050 rovibronic energy levels have been obtained from the 3713 values of the experimental wavenumbers. All the energy levels were obtained relative to the

lowest vibro-rotational level ( $v = 0, N = 0$ ) of the  $a^3\Sigma_g^+$  electronic state.

The shift  $(33.631 \pm 0.004) \text{ cm}^{-1}$  between uncoupled levels of ortho- and paradeuterium was obtained by the least squares analysis of the  $a^3\Sigma_g^+$ ,  $v = 0, N = 0 \div 18$  levels with odd and even values of the rotational quantum number  $N$ . According to [16] the difference  $E_{a01} - E_{a00} = (33.62 \pm 0.10) \text{ cm}^{-1}$ . Both values coincide within error bars, but our value is obtained with much higher precision. Taking into account the values of the SD uncertainties of our optimal level values (see table III), this increase of precision in obtaining the shift value is significant.

Optimal values of the rovibronic levels for the triplet electronic states corresponding to principle quantum numbers  $n = 2, 3$  of the united atom are listed in table III. Radiative transitions between those levels are located in visible part of spectra, which is most convenient for spectroscopic studies of non-equilibrium gases and plasmas [4, 5]. The expanded version of the table III including all 1050 optimal level values is presented in [46]. For each rovibronic level we introduced into the table III the standard deviation of the empirical determination (in brackets), the number of spectral lines  $n_\nu$  which originate or terminate on that level, and the difference  $\Delta E$  between energy level values reported in [16] and those obtained in the present work.

Several interesting things could be seen from the table III, namely:

i) In many cases the number of the lines, directly connected with certain level, is high enough for statistics. In some cases there are very few lines. In that cases the levels are obtained with less accuracy. It is important to stress, that the SD uncertainties of empirical determination of optimal level values partly reflect the influence of  $n_\nu$  on the SD values. This is the trend (not straightforward dependence) because there are more factors of the influence. The levels with  $n_\nu < 4$  should be considered as unreliable. The SD of such levels are mainly determined by experimental uncertainties of few lines directly connected with those levels. Additional experimental studies are needed to obtain more reliable results.

ii) The differences  $\Delta E$  are generally less, than the value  $0.05 \text{ cm}^{-1}$ , reported in [16] as SD uncertainty of the energy levels. This confirms our assumption that the unique SD uncertainty for all the levels declared in [16] is only an upper-limit estimate of real uncertainties of various levels.

iii) The vast majority of the  $\Delta E$  are much higher than SD error bars of our optimal values, which normally are within the range of  $0.004 \div 0.03 \text{ cm}^{-1}$  depending on the value of

rotational and vibrational quantum numbers. Thus, the deviations of the data reported in [16] from the optimal level values obtained in the present work are significant.

Currently it is not possible to find out and list reasons for those deviations for all and every levels, because [16] does not contain information about details of calculating the common differences in various bands. We may presume that they appeared as a result of following reasons: errors of reading from photo plates, round up errors in calculating the wavenumbers from measured wavelengths, lack of deconvolution of blended lines, subjective preferences in eliminating some of controversial experimental data, some additional assumptions (like neglecting  $\Lambda$  — doubling for some states), transfer and accumulation of experimental errors in the method of common differences adopted in [16] for wavenumber analysis of separate bands, quite subjective multi-step procedure of the analysis of the band systems. It is clear that for various rovibronic states all these factors may multiply or compensate each other.

Sometimes the nature of the differences  $\Delta E$  may be easily recognized. One typical example is illustrated in figure 8, in which the differences  $\Delta E$  are shown for rotational levels in the ground vibrational states ( $v = 0$ ) of the  $a^3\Sigma_g^+$  (d),  $c^3\Pi_u^-$  (c), and  $j^3\Delta_u^-$  (b) electronic states. The error bars represent our estimates (one SD) of the empirical determination of the optimal energy level values obtained by pure statistical approach in the present work. One may see that, as it was already mentioned, quite often the deviations  $\Delta E$  are less than  $0.05 \text{ cm}^{-1}$ , but significantly higher than SD uncertainties of optimal level values (figure 8(d)). In figure 8(b) and figure 8(c) one may see interesting behaviour of the deviation  $\Delta E$  — periodical changes for rotational level with odd and even values of  $N$  (for uncoupled levels of ortho- and para- molecules). Similar effect is observed for many other electronic-vibrational states including the case shown in figure 8(d).

Small alternations of the deviations  $\Delta E$  (less than  $0.1 \text{ cm}^{-1}$ ) are connected with the difference in the values of the shift between levels of ortho- and para- molecules obtained in the present work and in [16]. More pronounced cases of the alternations appear as a result of experimental errors due to non-optimal method of energy level derivation used in [16] — the sequential, multi-step procedure based on calculating common differences. The error appeared in one common difference due to one spurious experimental wavenumber value is transferred from previous energy level value to the next one. The mechanism is valid also for small random errors with various final results, because subsequent pairs of lines within a band may have experimental errors of various values and signs. Sometimes random errors



may partially compensate each other, but in principle this method has the possibility of an accumulation of experimental wavenumber errors and transferring them into the errors of the empirical values of rovibronic energy levels.

The typical example of the alternation appearance caused by spurious experimental wavenumber values is illustrated in figure 8(a,b,c). They demonstrate the influence of two significant errors in wavenumbers of the  $R$ -branch lines of the  $(0-0)$  band of the  $j^3\Delta_g^- - c^3\Pi_u^-$  electronic transition on the empirical values of the rotational levels obtained in [16] for the upper  $j^3\Delta_g^-$ ,  $v = 0$  and lower  $c^3\Pi_u^-$ ,  $0$  electronic-vibrational states of the band.

Excellent agreement between the observed and calculated wavenumbers reported in [16] seen in figure 8(a) is the evidence that the wavenumbers of the  $R4$  and  $R12$  spectral lines were used in determination of the level values. Experimental wavenumbers reported in [16] for both lines were classified as outliers by our statistical analysis. Results of our independent experiments confirmed that this is caused by occasional errors in [16]. The wavenumber values from [16] for the lines  $R4$  and  $R12$  are underestimated and overestimated, respectively (see figure 8(a) and table I). From the figure 8(b,c) one may see how those experimental errors are transferred into the wrong values of the empirical energy levels via sequential adding of the common differences  $\Delta'_2(N)$  and  $\Delta''_2(N)$  calculated for upper and lower rovibronic levels. The cases of appearance, accumulation and partial compensation of experimental errors may be found in figure 8(b,c).

Taking into account the results of our previous studies of some triplet states of  $H_2$  molecule [26] it is easy to expect that the Dunham series expansions with empirical molecular constants from [15, 25] have rather limited ability to describe rovibronic levels of the  $D_2$  isotopomer. These expectations were confirmed by the results of the present work. Typical example of the contradictions is illustrated in figure 9 representing the differences  $\Delta E$  between optimal values of the energy levels obtained in the present work and those calculated with molecular constants from [15, 25] for various rotational and vibrational levels of the  $a^3\Sigma_g^+$  electronic state of  $D_2$  molecule. One may see that the deviations show strong dependencies on vibrational and rotational quantum numbers, achieving values of about  $100 \text{ cm}^{-1}$ . It should be stressed that according to our previous studies of the potential curves [30] the  $a^3\Sigma_g^+$  electronic state is almost free from non-adiabatic effect of perturbations. Higher electronic states are mainly perturbed due to electronic-rotational and electronic-vibrational interactions, and simple Dunham expansions are non applicable.

For determination of precise absolute values of the triplet rovibronic levels of  $D_2$  it is desirable to make pure statistical analysis of all currently available experimental data on the wavenumbers of singlet rovibronic transitions and to use the data of anticrossing spectroscopy [49, 50, 51] for establishing the link between singlet and triplet state. The approach used in the present work is most appropriate for solving this problem in the future. Nowadays the absolute values of the triplet rovibronic levels (relative to the  $X^1\Sigma_g^+$ ,  $v = 0$   $N = 0$  ground rovibronic state) may be obtained only by adding an absolute value  $E_{a00}$  of energy of the  $a^3\Sigma_g^+$ ,  $v = 0$   $N = 0$  rovibronic level to the relative energy level values obtained in the present work. According to [16]  $E_{a00} = 95348.2(4) \text{ cm}^{-1}$ , while in [52]  $E_{a00} = 95348.3(1) \text{ cm}^{-1}$ . These values coincide within the uncertainties reported in original papers and may be used. The precision of such absolute calibration should be better than  $1 \text{ cm}^{-1}$ .

Our relative values of triplet rovibronic levels of  $D_2$  molecule may be used not only in comparisons with results of non-empirical calculations. They are recommended for accurate calculating the wavenumbers of triplet-triplet optical transitions for computer simulations of emission and absorption spectra in applied spectroscopy of non-equilibrium gases and plasmas. Moreover, the high precision of optimal level values achieved in the present work provides the opportunity to expand existing identification of triplet rovibronic lines by accurate calculating wavenumbers of all currently unassigned rovibronic transitions allowed by the selection rules for electric dipole transitions and detecting corresponding lines in experimental spectra. From the Grotrian diagram of the  $D_2$  molecule it may be seen that several new band systems may be discovered and investigated.

### Acknowledgments

The authors are indebted to Prof. S. Ross for providing the electronic version of the wavelength tables for lines of the  $D_2$  emission spectrum measured and assigned by G.H. Dieke and co-workers (Appendix C. from Ref.[16]), and to Mr. M.S. Ryazanov for development of the computer code and helpful discussions. This work was supported, in part, by the Russian Foundation for Basic Research (the Grant #06-03-32663a).

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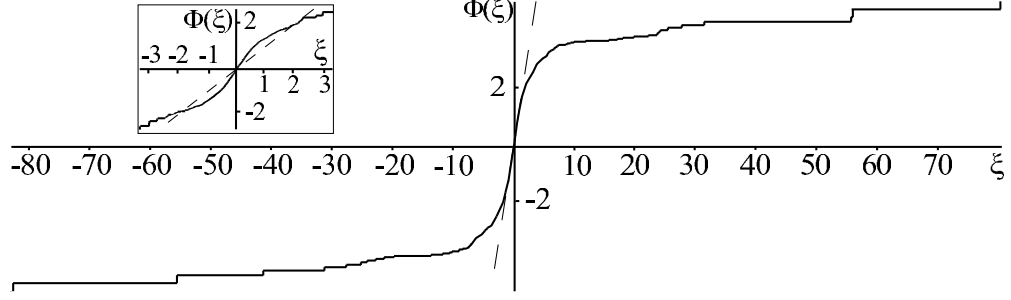


FIG. 1: Empirical function  $\Phi(\xi)$  obtained when all published experimental data with RMS uncertainties equal to the error estimates reported in original papers. The onset represents the central part of the  $\Phi(\xi)$  in larger scale.

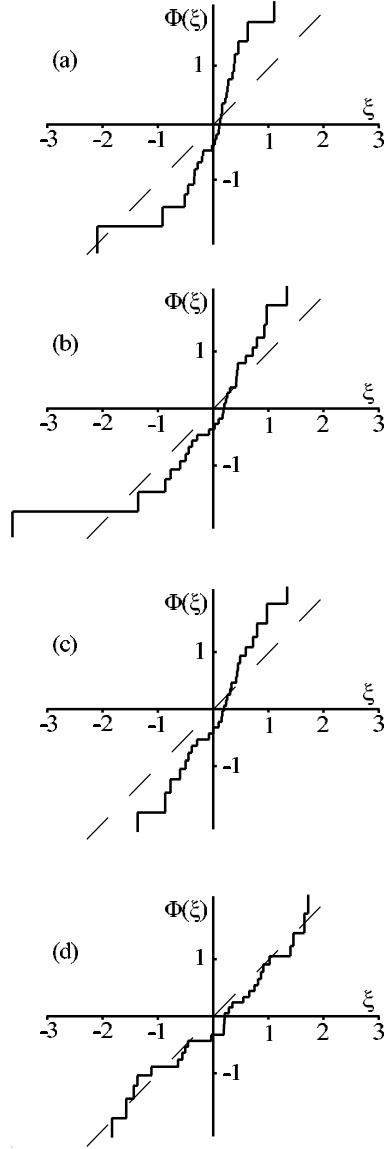


FIG. 2: Empirical functions  $\Phi^{(m)}(\xi)$  obtained in different  $m$ -th iterations (a, b, c, and d correspond to  $m = 1, 2, 3$ , and 4) of the statistical analysis of the sample of experimental data representing wavenumbers of R- and P- branch lines of the  $(0-1)$  band of the  $e^3\Sigma_u^+ - a^3\Sigma_g^+$  electronic transition of  $D_2$ .

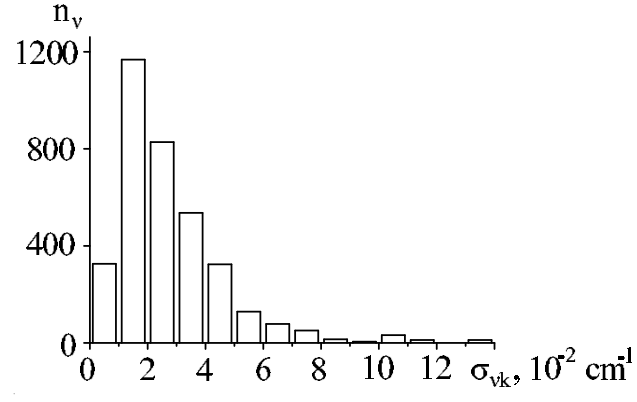


FIG. 3: The amount of the wavenumber values  $n_\nu$  within various enlarged samples of the uniformly precise experimental data.



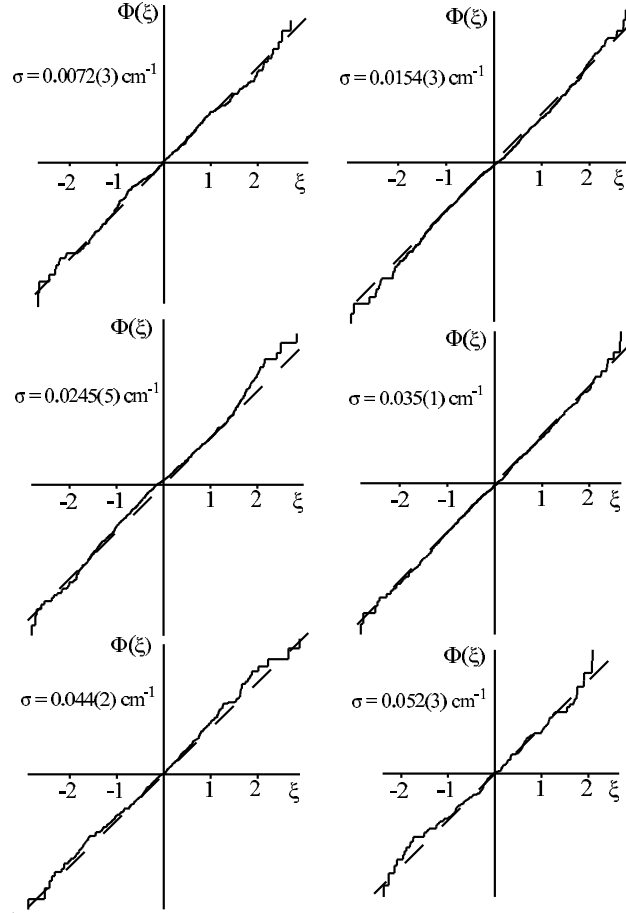


FIG. 4: Empirical functions  $\Phi(\xi)$  representing the error distributions within the first six enlarged samples corresponding to the intervals  $(0 \div 0.01)$ ,  $(0.01 \div 0.02)$ ,  $(0.02 \div 0.03)$ ,  $(0.03 \div 0.04)$ ,  $(0.04 \div 0.05)$ ,  $(0.05 \div 0.06)$  (from left to right, from top to bottom). The values of the experimental uncertainty obtained in the present work for every sample are shown near appropriate graphs together with SD of their statistical determination (in brackets).

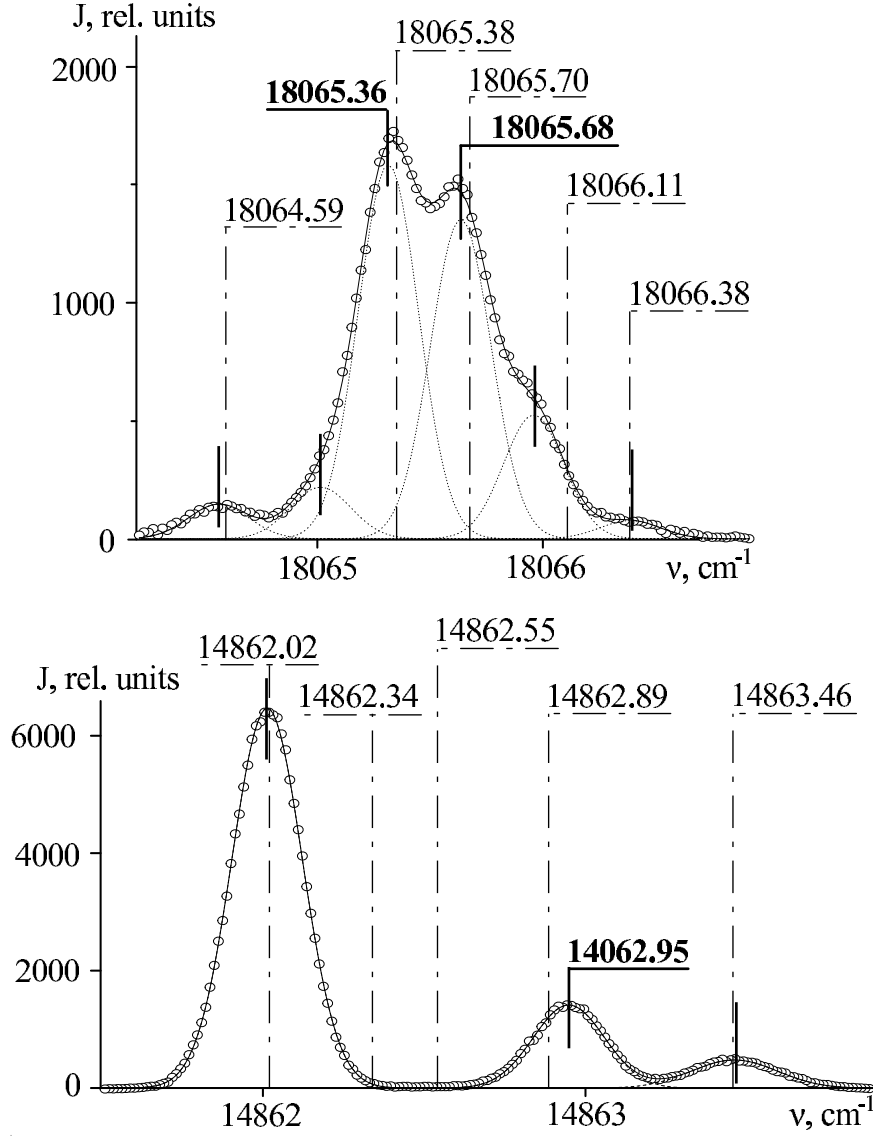


FIG. 5: Fragments of the  $D_2$  spectrum in the neighbourhood of the questionable lines. Experimental intensity  $J$  in relative units is shown by open circles. Dotted lines represent Gaussian profiles for separate lines obtained by deconvolution, while solid line corresponds to the total intensity obtained by summing over the components. The wavenumber values from the Appendix C of [16] are shown and marked by dash-dot vertical lines. Pieces of bold vertical lines denote maxima of the separate line profiles. Bold underlined wavenumbers represent the new wavenumber values for the questionable lines obtained in the present work.

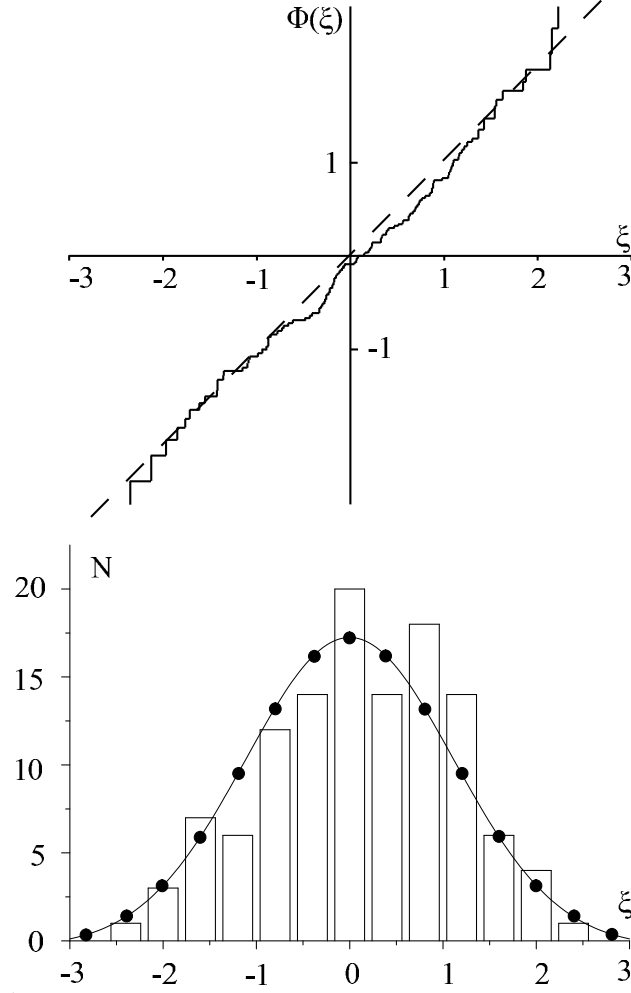


FIG. 6: Empirical function  $\Phi(\xi)$  for the sample containing new wavenumber values for questionable lines. The frequency diagram  $N$  versus  $\xi$  is constructed with uniform width intervals equal to 0.4.  $N$  represents the number of the deviations  $\xi_{ij}$  within each interval. The columns show experimental results while the solid line with circles corresponds to the normal distribution with zero mean and variance equal to unity.

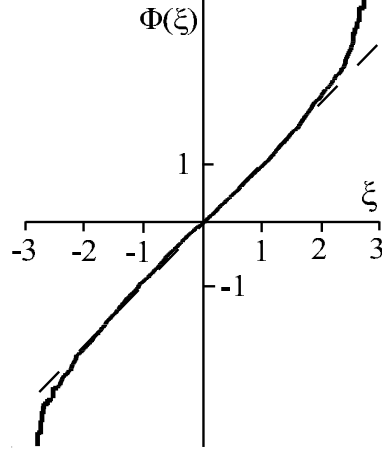


FIG. 7: Empirical function  $\Phi(\xi)$  obtained for the final set of all available experimental data (see the text) with RMS errors estimates obtained in the present work by the statistical analysis.

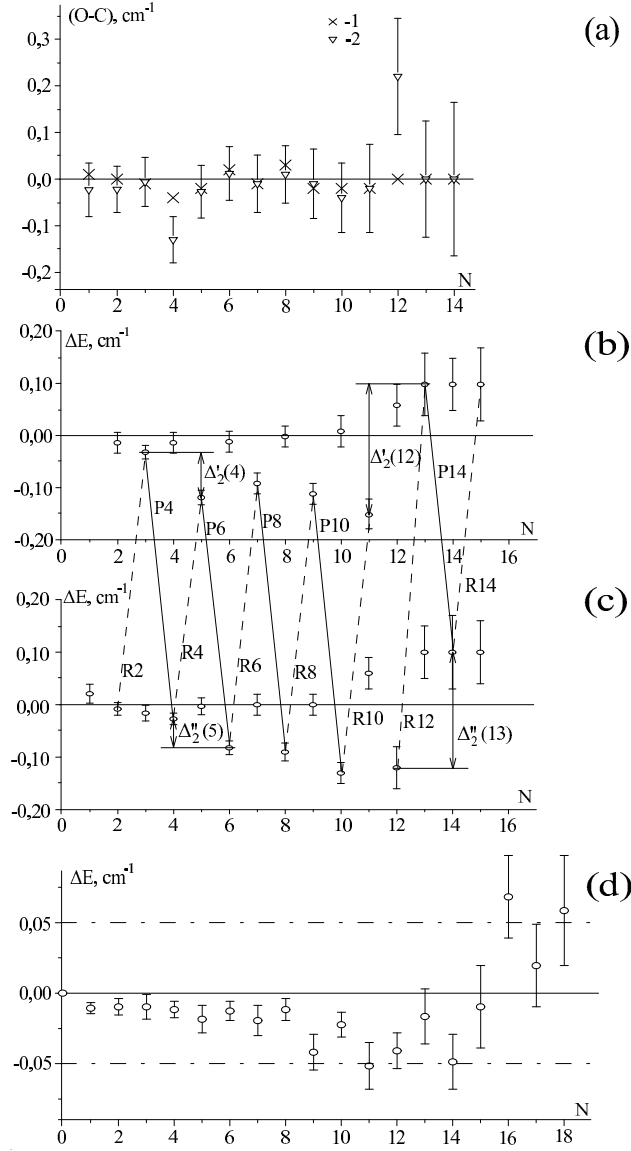


FIG. 8: The differences  $(O - C)$  between observed wavenumbers from [16] and those calculated as the differences of empirical levels from [16] (1) and of the optimal level values (2) for  $R$ -branch lines of the  $(0 - 0)$  band of the  $j^3\Delta_u^- - c^3\Pi_u^-$  electronic transition (a). The error bars in figure (a) represent the sum of standard deviations for optimal values of upper and lower levels and for the wavenumber value (obtained in the present work for the set of experimental data from [16] belonging to this band). The differences  $\Delta E$  between the level values from [16] and the optimal level values (Table III) for various rotational levels of the  $j^3\Delta_u^-$ ,  $v = 0$  (b);  $c^3\Pi_u^-$ ,  $v = 0$  (c); and  $a^3\Sigma_g^+$ ,  $v = 0$  (d) electronic-vibrational states of  $D_2$  molecule. Spectral lines of the  $R$ - and  $P$ -branches of the  $(0-0)$  band of the  $j^3\Delta_u^- - c^3\Pi_u^-$  electronic transition connecting some of the levels are shown by vertical lines (dashed for  $R$ -branch and solid for  $P$ -branch) with standard labels. The error bars in figures (b), (c) and (d) represent SD of the optimal energy levels obtained in the present work. Horizontal solid lines represent zero level, and horizontal dash-dotted lines — error

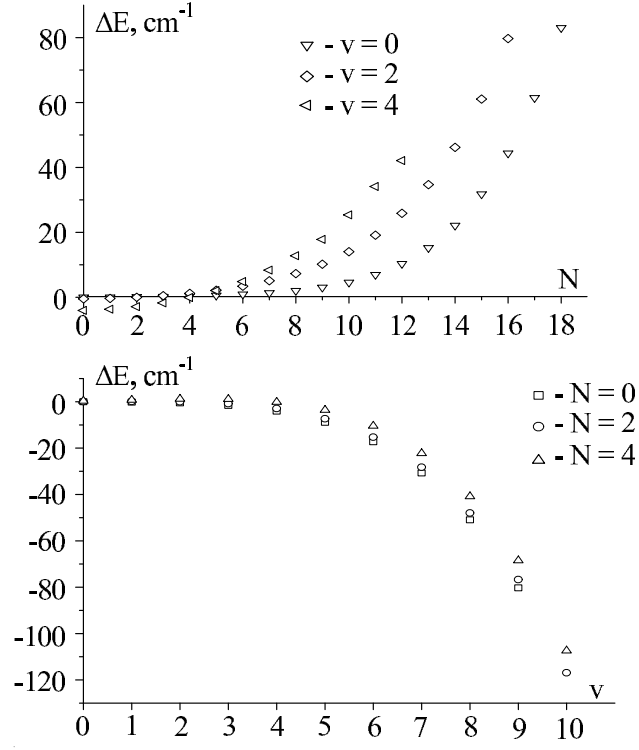


FIG. 9: The differences  $\Delta E$  between optimal values of the energy levels obtained in the present work and those calculated with molecular constants from [25] for various rotational and vibrational levels of the  $a^3\Sigma_g^+$  electronic state of  $D_2$  molecule.

TABLE I: Experimental values of the wavenumbers (in  $\text{cm}^{-1}$ ) of some spectral lines of  $D_2$  obtained in the present work (P.W.) and those reported in [16]. O-C denotes the differences between Observed wavenumber values and those Calculated as differences of corresponding optimal energy level values obtained in the present work.

Electronic transition	Band	Line	[16]	O-C	P.W.	O-C
$e^3\Sigma_u^+ - a^3\Sigma_g^+$	2-0	P11	13751.08	-0.14	13751.29	0.07
	3-0	R6	15868.98	-0.05	15869.01	-0.02
		R9	15705.21	0.23	15704.98	0.00
	4-1	P8	14862.89	-0.08	14862.95	-0.02
	5-2	P6	14524.31	0.07	14524.26	0.02
	6-2	R4	15977.48	-0.06	15977.56	0.02
	6-3	P9	13703.95	0.09	13703.87	0.01
	7-3	P5	15107.67	-0.04	15107.71	0.00
	8-3	R0	16354.21	0.05	16354.19	0.03
	8-4	P5	14468.77	-0.10	14468.86	-0.01
		R3	14727.33	-0.06	14727.38	-0.01
	9-5	P4	13861.27	-0.19	13861.45	-0.01
		R4	14002.82	-0.11	14002.91	-0.02
	10-4	P4	16124.14	0.25	16123.94	0.05
	1-1	R2	20346.49	0.07	20346.42	0.00
	1-2	R0	18564.54	0.21	18564.19	-0.14
$f^3\Sigma_u^+ - a^3\Sigma_g^+$	2-1	P3	21653.13	0.20	21653.04	0.11
	2-3	P3	18242.42	0.09	18242.40	0.07
	0-1	R9	15019.54	0.10	15019.44	0.00
	1-0	P2	18207.70	0.10	18207.60	0.00
$d^3\Pi_u - a^3\Sigma_g^+$		P5	18065.38	0.06	18065.36	0.04
	1-1	Q1	16460.87	-0.07	16460.93	-0.01
		Q10	16267.60	-0.05	16267.64	-0.01
	1-2	Q10	14582.86	0.03	14582.84	0.01
	2-0	Q1	19823.53	0.09	19823.45	0.01
	2-1	R1	18065.70	0.07	18065.68	0.05
		R5	18109.66	0.04	18109.64	0.02
		R6	18107.89	-0.04	18107.97	0.04

**table I.** (Continued.)

Electronic transition	Band	Line	[16]	O-C	This work	O-C
$d^3\Pi_u - a^3\Sigma_g^+$	4-3	P3	17401.87	0.11	17401.74	-0.02
		R6	17586.74	0.07	17586.69	0.02
	4-5	Q7	14280.99	0.06	14280.94	0.01
	5-2	Q3	20510.44	-0.14	20510.57	-0.01
	5-3	Q6	18757.31	-0.17	18757.49	0.01
		Q8	18677.56	0.08	18677.49	0.01
	6-4	Q7	18420.01	-0.11	18420.10	-0.02
	7-6	Q5	16727.50	0.18	16727.38	0.06
$k^3\Pi_u - a^3\Sigma_g^+$	0-0	P8	21966.23	-0.01	21966.21	-0.03
		Q8	22180.52	0.16	22180.39	0.03
		R6	22452.89	0.17	22452.75	0.03
	0-1	Q8	20406.67	-0.04	20406.68	-0.03
		R3	20613.91	0.19	20613.78	0.06
	1-2	P4	20217.44	0.11	20217.32	-0.01
	2-3	P2	20142.72	-0.14	20142.76	-0.10
		R2	20282.53	0.21	20282.45	0.13
		R4	20320.54	0.09	20320.48	0.03
	3-3	Q6	21592.35	0.22	21592.11	-0.02
	4-3	R4	23156.99	0.10	23156.92	0.03
	4-5	P5	19755.38	-0.15	19755.42	-0.11
	5-4	Q4	22761.98	-0.13	22762.13	0.02
	1-2	Q5	22881.68	-0.05	22881.71	-0.02
		P3	22670.82	-0.12	22670.88	-0.06
$n^3\Pi_u - a^3\Sigma_g^+$	3-3	P4	16779.23	-0.09	16779.32	0.00
$h^3\Sigma_g^+ - c^3\Pi_u$	0-0	P5	16588.93	0.13	16588.87	0.07
$g^3\Sigma_g^+ - c^3\Pi_u$	0-1	P3	15064.96	-0.18	15065.27	0.13
	1-1	P4	16502.17	0.13	16502.08	0.04
	2-1	P5	17846.80	-0.27	17847.07	0.00
	2-2	P6	16164.95	0.22	16164.69	-0.04
		R9	16314.06	0.01	16314.07	0.02
		Q10	16045.63	-0.03	16045.64	-0.02



**table I.** (Continued.)

Electronic transition	Band	Line	[16]	O-C	This work	O-C
$i^3\Pi_g^- - c^3\Pi_u$	0-0	P7	16787.90	-0.10	16787.97	-0.03
		P14	16369.80	-0.08	16369.84	-0.04
		Q3	17071.29	-0.09	17071.28	-0.10
		Q9	16898.78	0.13	16898.69	0.04
		R9	17150.62	0.17	17150.53	0.08
		R12	17109.51	-0.09	17109.64	0.04
	1-0	P3	18525.88	0.22	18525.72	0.06
		Q3	18598.23	-0.27	18598.59	0.09
	2-1	R1	18451.87	0.23	18451.64	0.00
		R2	18464.46	0.13	18464.34	0.01
	2-2	P10	16345.66	-0.04	16345.72	0.02
		R4	16864.08	0.21	16863.92	0.05
		R8	16857.89	-0.59	16858.46	-0.02
	2-3	Q3	15207.72	0.05	15207.75	0.08
	3-3	P3	16517.58	0.06	16517.57	0.05
		Q2	16599.70	0.05	16599.70	0.05
		R5	16693.01	-0.16	16693.13	-0.04
$j^3\Delta_g^+ - c^3\Pi_u$	0-0	P13	17309.93	-0.02	17309.93	-0.02
		Q12	17667.66	0.00	17667.68	0.02
	1-0	Q2	19060.17	0.14	19060.15	0.12
	1-1	P10	17192.24	0.02	17192.26	0.04
		Q7	17439.67	0.11	17439.65	0.09
		R8	17722.82	-0.04	17722.82	-0.04
	2-1	Q5	18907.85	-0.11	18907.90	-0.06
	2-2	P9	17081.06	-0.10	17081.14	-0.02
$j^3\Delta_g^- - c^3\Pi_u$	0-0	P14	17182.21	-0.01	17182.26	0.04
		Q13	17564.20	-0.02	17564.24	0.02
		R4	17654.95	-0.13	17655.06	-0.02
		R12	17922.15	0.22	17921.87	-0.06
	1-0	P7	18863.60	0.26	18863.37	0.03
		Q4	19066.14	-0.18	19066.26	-0.06

TABLE II: The amounts of various kinds of the experimental data reported in various original papers and obtained in the present work (P.W.): total *reported*, *useable* for the statistical analysis, *excluded* as the outliers, *used* for determination of optimal level values, and the rate of used lines in %.

Reference	[16]	[32]	[31]	[28]	[34]	[33]	[29]	[35]	P.W.	Total
reported	3117	350	285	81	37	83	3	1	125	4082
useable	3053	350	285	81	37	12	3	1	125	3947
excluded	179	18	18	5	4	10	0	0	0	234
used	2874	332	267	76	33	2	3	1	125	3713
%	94.1	94.9	93.7	93.8	89.2	16.7	100	100	100	94.1

TABLE III: Optimal values  $E_{nvN}$  of rovibronic energy levels (in  $\text{cm}^{-1}$ ) for various triplet electronic states of  $D_2$  molecule obtained in the present work. The uncertainties of the  $E_{nvN}$  value determination (one SD) are shown in brackets in units of last significant digit.  $n_\nu$  — the number of various spectral lines directly connected with certain level.  $\Delta E$  is the difference between energy level values obtained in the present work and those reported in [16].

$(1s\sigma 2s\sigma)a^3\Sigma_g^+$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	0	21	0	1814.908(5)	25	-0.008	3560.726(6)	26	-0.016
1	33.631(4)	43	-0.011	1847.364(8)	55	-0.014	3592.036(8)	56	-0.016
2	100.770(6)	52	-0.010	1912.172(5)	66	-0.012	3654.573(5)	70	-0.003
3	201.109(9)	47	-0.009	2009.042(8)	63	-0.002	3748.034(8)	64	-0.004
4	334.333(6)	49	-0.013	2137.628(6)	57	-0.008	3872.103(6)	64	-0.003
5	499.850(10)	37	-0.020	2297.385(9)	46	-0.005	4026.245(9)	49	-0.005
6	697.092(7)	30	-0.012	2487.748(6)	42	0.002	4209.894(7)	44	0.006
7	925.260(11)	19	-0.020	2707.967(10)	27	-0.007	4422.319(10)	25	0.001
8	1183.573(8)	19	-0.013	2957.220(7)	27	0.020	4662.756(7)	22	0.014
9	1471.063(13)	11	-0.043	3234.634(11)	21	-0.004	4930.308(11)	14	-0.008
10	1786.713(9)	12	-0.023	3539.206(8)	15	0.024	5224.035(9)	10	0.015
11	2129.524(17)	6	-0.054	3869.902(14)	6	0.008	5542.94(2)	4	-0.010
12	2498.252(13)	6	-0.042	4225.651(16)	3	0.069	5885.90(3)	3	0.010
13	2891.75(2)	5	-0.019	4605.20(2)	3	-0.010	6251.85(3)	2	0.040
14	3308.86(2)	5	-0.050	5007.43(3)	3	-0.050	6639.59(3)	2	0.020
15	3748.44(3)	5	-0.010	5431.37(3)	3	0.010	7048.04(3)	2	0.030
16	4208.73(3)	5	0.070	5875.16(4)	2	0.050	7475.59(17)	2	0.050
17	4689.10(3)	4	0.010	6338.32(4)	2	0.040			
18	5187.38(4)	3	0.060	6818.59(4)	2	0.080			
v = 3				v = 4			v = 5		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	5238.994(6)	27	-0.014	6851.077(6)	21	-0.007	8398.070(7)	14	-0.000
1	5269.198(8)	54	-0.008	6880.190(9)	48	0.000	8426.100(9)	37	0.000
2	5329.503(6)	64	-0.013	6938.313(6)	57	-0.013	8482.065(6)	37	0.015

**table III.** (Continued.)

$(1s\sigma 2s\sigma)a^3\Sigma_g^+$									
v = 6			v = 7			v = 8			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	9880.806(11)	10	-0.016	11299.845(16)	6	-0.045	12655.467(18)	5	-0.007
1	9907.775(10)	26	0.005	11325.784(11)	18	-0.004	12680.356(12)	12	-0.036
2	9961.617(7)	32	-0.017	11377.500(8)	18	0.000	12729.972(9)	13	-0.052
3	10042.093(10)	28	-0.013	11454.821(12)	14	-0.010	12804.129(13)	14	-0.059
4	10148.876(7)	28	-0.026	11557.399(9)	14	-0.009	12902.503(9)	13	-0.143
5	10281.509(10)	25	-0.069	11684.766(13)	8	-0.036	13024.059(14)	4	-0.049
6	10439.463(8)	20	-0.033	11836.493(10)	7	-0.033	13170.42(5)	2	-0.000
7	10622.101(13)	12	-0.071	12011.941(19)	3	-0.051			
8	10828.794(13)	7	-0.084	12210.76(3)	2	-0.060			
9	11057.80(2)	2	0.010						
10									
11	11594.7(3)	2	-						
12	11894.2(3)	2	-						
v = 9			v = 10						
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
0	13947.39(4)	1	0.000						
1	13971.355(15)	4	-0.035	15198.29(5)	2	-0.030			
2	14018.883(12)	4	-0.013	15243.76(5)	2	-0.020			
3	14089.876(15)	3	0.024	15311.62(5)	2	-0.040			
4	14184.038(13)	4	-0.088	15401.72(7)	1	0.010			
5	14300.933(17)	3	0.017	15513.75(5)	2	-0.050			
6	14440.112(13)	1	0.028						
$(1s\sigma 2p\pi)c^3\Pi_u^-$									
v = 0			v = 1			v = 2			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	-132.611(18)	12	0.021	1548.794(14)	9	0.036	3168.223(11)	8	0.087
2	-71.553(12)	17	-0.007	1607.788(9)	15	0.032	3225.211(8)	12	0.079

**table III.** (Continued.)

$(1s\sigma 2p\pi)c^3\Pi_u^-$									
v = 3				v = 4			v = 5		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	4727.022(9)	7	0.108	6226.366(19)	3	0.144	7667.225(13)	3	0.125
2	4782.112(9)	10	0.038	6279.454(11)	7	0.096	7718.429(10)	2	0.141
3	4864.307(13)	11	0.073	6358.796(14)	4	0.084	7794.944(13)	2	0.116
4	4973.456(10)	12	0.054	6464.117(13)	4	0.063	7896.475(10)	2	-0.035
5	5109.097(16)	9	0.093	6594.990(18)	4	0.050			
6	5270.732(15)	5	0.028						
7	5457.84(2)	5	-0.010						
8	5669.46(2)	4	0.030						
9	5905.35(3)	1	-0.020						
10	6164.52(3)	1	0.080						
v = 6									
N	$E_{nvN}$	$n_\nu$	$\Delta E$						
1	9050.44(2)	1	-						
2	9099.750(17)	1	-						
3	9173.43(2)	1	-						
4	9271.249(18)	1	-						
$(1s\sigma 2p\pi)c^3\Pi_u^+$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	-132.586(12)	22	-0.004	1548.813(9)	16	0.017	3168.273(7)	13	0.037
2	-71.584(14)	26	0.014	1607.790(12)	19	0.040	3225.247(10)	17	0.123
3	19.662(11)	28	-0.032	1695.990(8)	21	0.040	3310.490(9)	16	0.030
4	140.727(15)	27	-0.026	1813.023(13)	18	0.047	3423.541(11)	14	0.079
5	291.217(12)	24	-0.087	1958.482(10)	18	0.038	3564.085(8)	14	0.095
6	470.542(16)	19	-0.022	2131.814(15)	14	0.016	3731.563(12)	8	0.057
7	678.114(15)	15	-0.094	2332.393(14)	9	-0.003	3925.279(18)	9	0.051
8	913.12(2)	10	0.022	2559.53(2)	5	0.060	4144.65(2)	4	0.140

**table III.** (Continued.)

$(1s\sigma 2p\pi)c^3\Pi_u^+$									
v = 3				v = 4			v = 5		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	4727.078(7)	14	0.052	6226.429(10)	7	0.081	7667.297(13)	2	0.053
2	4782.081(12)	16	0.109	6279.553(10)	9	0.007	7718.544(13)	2	0.016
3	4864.446(8)	15	0.014	6359.007(11)	7	0.133	7795.177(10)	1	-
4	4973.606(14)	9	0.084	6464.401(14)	8	0.079	7896.833(13)	1	-
5	5109.368(10)	10	0.092	6595.379(13)	6	-0.009	8023.166(10)	1	-
6	5271.03(2)	5	0.110	6751.361(18)	4	0.059			
7	5458.145(18)	7	0.035						
8	5670.02(3)	5	-0.030						
9	5905.61(2)	3	0.070						
v = 6				v = 7					
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
1	9050.47(2)	1	-	10376.62(2)	1	-			
2	9099.88(2)	1	-	10424.20(2)	1	-			
3	9173.710(17)	1	-	10495.262(18)	1	-			
4	9271.63(2)	1	-	10589.37(2)	1	-			
5	9393.409(18)	1	-	10706.613(18)	1	-			
$(1s\sigma 3s\sigma)h^3\Sigma_g^+$									
v = 2				v = 3			v = 4		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	20071.893(17)	1	0.037	21588.238(10)	1	0.052	23042.197(13)	2	0.083
1	20101.320(16)	2	0.100	21615.731(12)	2	0.099	23068.46(2)	2	0.143
2	20160.107(13)	2	0.053	21670.798(8)	3	0.032	23120.982(10)	4	0.088
3	20247.847(15)	3	0.113	21752.929(13)	3	0.061	23199.357(13)	4	0.083
4	20364.077(13)	2	0.063	21861.839(9)	3	0.051	23303.289(13)	3	-0.009
5							23432.221(16)	3	0.059

**table III.** (Continued.)

$(1s\sigma 3p\sigma)e^3\Sigma_u^+$									
v = 0			v = 1			v = 2			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	11649.190(14)	5	-0.010	13137.502(10)	6	-0.012	14558.258(12)	6	0.002
1	11676.174(8)	12	-0.004	13163.431(6)	12	-0.011	14583.137(7)	14	0.003
2	11730.037(13)	12	-0.007	13215.170(9)	15	-0.010	14632.770(11)	13	0.000
3	11810.600(9)	17	-0.020	13292.570(7)	16	-0.010	14707.003(8)	15	-0.003
4	11917.524(12)	12	-0.004	13395.293(10)	11	-0.003	14805.515(11)	14	0.015
5	12050.485(9)	12	0.005	13523.013(7)	12	0.007	14927.986(8)	14	-0.006
6	12208.941(13)	8	-0.021	13675.191(10)	12	-0.001	15073.923(11)	12	-0.013
7	12392.375(9)	8	0.005	13851.369(8)	11	0.011	15242.814(8)	13	0.016
8	12600.117(13)	6	-0.017	14050.868(11)	9	-0.018	15434.079(13)	8	-0.039
9	12831.480(11)	5	-0.030	14272.987(8)	10	0.003	15646.946(10)	8	0.024
10	13085.653(16)	5	-0.043	14517.021(13)	6	-0.021	15880.745(15)	5	0.005
11	13361.853(12)	4	-0.013	14782.091(10)	5	-0.001	16134.676(15)	3	0.044
12	13659.139(19)	4	-0.019	15067.365(16)	3	0.015	16407.97(10)	2	-0.060
13	13976.603(17)	3	-0.043	15371.957(16)	5	-0.007	16696.56(5)	2	-0.030
14	14313.27(2)	3	0.000	15694.80(2)	4	0.030	17003.73(4)	2	0.010
15	14668.18(3)	2	-0.050	16035.06(3)	4	0.050	17326.48(5)	2	0.070
16	15040.49(3)	2	0.010	16391.90(3)	4	0.010	17675.65(3)	1	0.010
17	15428.58(4)	2	0.050	16763.73(4)	4	0.060			
18	15832.13(3)	2	0.020	17150.23(4)	2	0.040			
19	16249.09(4)	2	0.060	17549.32(5)	1	0.080			
v = 3			v = 4			v = 5			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	15911.178(10)	7	-0.018	17195.132(10)	10	-0.002	18408.097(10)	7	-0.007
1	15934.967(6)	19	-0.057	17217.850(6)	17	0.000	18429.790(6)	16	-0.010
2	15982.471(9)	20	-0.001	17263.194(8)	17	-0.004	18473.084(9)	15	-0.006
3	16053.509(6)	19	-0.009	17331.018(6)	19	0.002	18537.934(7)	14	-0.034
4	16147.768(9)	19	0.012	17420.989(9)	18	-0.008	18624.360(9)	14	0.010
5	16264.946(6)	18	-0.006	17532.827(6)	17	-0.007	18734.130(6)	14	-0.010

**table III.** (Continued.)

$(1s\sigma 3p\sigma)e^3\Sigma_u^+$									
v = 6				v = 7			v = 8		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	19546.641(11)	7	-0.001	20605.338(10)	8	-0.008	21575.310(13)	9	-0.030
1	19567.047(7)	16	-0.007	20624.515(6)	15	-0.015	21593.153(7)	19	-0.013
2	19607.728(10)	16	-0.008	20662.787(9)	16	-0.017	21628.745(10)	19	-0.005
3	19668.569(7)	16	0.001	20720.289(6)	14	-0.009	21681.957(7)	20	-0.007
4	19749.319(10)	16	-0.019	20795.613(9)	12	-0.023	21752.568(11)	18	-0.038
5	19849.642(8)	15	-0.012	20889.773(6)	14	-0.003	21840.510(8)	16	-0.010
6	19969.098(11)	14	-0.028	21001.748(10)	9	-0.008	21946.349(12)	7	-0.029
7	20107.185(7)	12	0.005	21131.071(7)	9	-0.001	22074.088(14)	2	0.002
8	20263.354(13)	8	0.006						
9				21440.901(17)	1	0.029			
v = 9				v = 10					
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
0	22442.451(11)	8	-0.011	23181.37(2)	4	0.004			
1	22458.482(7)	17	-0.002	23195.302(13)	11	-0.022			
2	22490.446(10)	16	-0.006	23223.064(16)	10	-0.024			
3	22538.192(7)	18	-0.002	23264.357(13)	11	-0.017			
4	22601.388(10)	18	-0.038	23318.792(19)	6	-0.042			
5	22679.660(7)	14	-0.040	23385.89(2)	3	-0.030			
6	22772.422(11)	10	-0.022						
7	22879.133(11)	3	0.037						
$(1s\sigma 3p\pi)d^3\Pi_u^-$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	16695.750(14)	4	-0.010	18308.303(11)	7	-0.033	19857.067(10)	8	0.003
2	16755.305(11)	5	-0.005	18365.680(8)	5	-0.010	19912.363(7)	8	-0.023
3	16844.286(15)	4	-0.006	18451.471(11)	7	-0.001	19995.024(10)	8	-0.014
4	16962.446(11)	4	-0.006	18565.354(8)	7	-0.004	20104.741(7)	8	-0.011



**table III.** (Continued.)

$(1s\sigma 3p\pi)d^3\Pi_u^-$									
v = 3			v = 4			v = 5			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	21343.645(12)	9	0.005	22769.442(12)	8	-0.012	24135.655(10)	10	0.005
2	21396.902(9)	8	-0.002	22820.678(8)	8	0.002	24184.948(7)	10	-0.008
3	21476.477(12)	8	-0.007	22897.296(12)	7	-0.006	24258.610(10)	9	0.000
4	21582.138(9)	8	-0.008	22998.963(8)	8	-0.013	24356.367(7)	9	-0.017
5	21713.423(13)	7	-0.013	23125.264(12)	8	-0.004	24477.809(11)	7	-0.029
6	21869.803(9)	8	0.057	23275.747(9)	7	0.003	24622.462(9)	9	-0.012
7	22050.667(15)	4	-0.007	23449.760(17)	5	-0.020	24789.747(12)	7	-0.007
8	22255.379(12)	4	0.011	23646.709(11)	6	-0.009	24979.060(12)	6	-0.010
9	22483.185(19)	2	-0.035	23865.26(2)	2	-0.005	25188.91(2)	3	0.010
10	22733.258(15)	3	0.002	24106.31(3)	2	0.020	25420.32(3)	2	0.040
11	23004.67(5)	2	-0.050	24367.28(6)	1	-0.030			
12	23293.59(6)	2	-0.010	24645.28(7)	1	-0.010			
13	23603.42(6)	1	0.030						
14	23930.61(6)	1	0.090						
v = 6			v = 7			v = 8			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	25443.364(10)	9	-0.004	26693.448(12)	6	-0.008	27886.595(13)	6	-0.005
2	25490.706(7)	9	-0.006	26738.891(9)	6	-0.021	27930.152(9)	6	0.008
3	25561.485(11)	8	-0.005	26806.814(12)	6	-0.014	27995.235(13)	6	0.035
4	25655.396(7)	8	-0.006	26896.934(9)	5	-0.054	28081.598(10)	6	-0.028
5	25772.049(11)	9	-0.019	27008.83(2)	5	-0.026	28188.852(15)	6	-0.072
6	25910.990(8)	7	-0.020	27142.454(10)	3	-0.024	28316.512(10)	5	0.008
7	26071.762(19)	3	-0.082	27296.310(15)	2	-0.070			
8	26253.93(3)	2	-0.080	27470.81(4)	1	-0.060			
v = 9			v = 10						
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
1	29023.33(5)	4	-0.040	30103.98(4)	2	-0.050			

**table III.** (Continued.)

$(1s\sigma 3p\pi)d^3\Pi_u^+$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	16695.884(8)	8	-0.014	18308.374(7)	12	0.006	19857.301(6)	15	-0.011
2	16755.611(11)	8	-0.011	18365.854(9)	14	-0.004	19912.998(10)	12	0.002
3	16844.912(9)	8	-0.002	18451.709(7)	13	-0.019	19996.263(6)	16	-0.013
4	16963.424(13)	5	-0.004	18565.166(10)	13	0.004	20106.670(9)	14	0.000
5	17110.685(9)	4	-0.005	18703.797(7)	12	-0.017	20243.786(7)	12	-0.006
6	17286.063(13)	4	-0.013	18884.047(15)	3	-0.007	20407.009(11)	7	0.001
7	17488.918(10)	4	0.002	19076.671(10)	4	0.009	20595.676(8)	6	0.004
8	17718.453(14)	4	-0.023	19297.282(14)	4	-0.002	20809.051(12)	5	-0.011
9	17973.850(12)	3	-0.030	19543.237(11)	3	0.023	21046.331(10)	4	-0.001
10	18254.078(18)	3	-0.048				21306.503(13)	3	-0.023
11	18557.648(15)	2	-0.078				21588.485(18)	1	0.015
12	18885.46(2)	1	-0.050				21891.41(3)	1	-0.010
v = 3				v = 4					
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
1	21343.795(7)	15	-0.005	22769.695(7)	14	-0.015			
2	21397.294(11)	14	0.006	22821.398(10)	15	0.002			
3	21477.206(7)	16	0.004	22898.632(7)	15	-0.012			
4	21583.081(11)	14	-0.001	23000.957(10)	16	-0.007			
5	21714.214(8)	14	0.006	23127.895(7)	15	-0.005			
6	21868.935(14)	5	-0.025	23278.629(11)	14	0.001			
7	22046.649(17)	1	-0.009	23451.647(9)	11	0.003			
$(1s\sigma 3d\sigma)g^3\Sigma_g^+$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
0	16716.76(3)	2	0.040	18225.643(18)	1	0.017	19649.58(3)	2	0.030
1	16731.26(2)	5	0.009	18242.564(13)	6	0.046	19662.30(2)	4	0.070
2	16761.132(14)	9	-0.022	18269.116(9)	9	0.034	19690.525(19)	6	0.045

**table III.** (Continued.)

$(1s\sigma 3d\sigma)g^3\Sigma_g^+$									
v = 3				v = 4					
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
0	20982.138(17)	1	0.052						
1	20996.599(14)	3	0.091						
2	21027.241(9)	6	0.029	22276.495(14)	3	0.085			
3	21075.984(15)	6	0.156	22327.149(19)	2	0.001			
4	21144.762(10)	6	0.038	22397.125(17)	2	0.125			
5	21234.849(15)	4	0.071	22487.30(2)	1	0.079			
6	21347.112(15)	3	0.108	22598.58(2)	1	-0.010			
7	21481.78(5)	2	0.070						
8	21639.07(3)	1	0.030						
9	21818.86(3)	1	-0.030						
10	22020.93(3)	1	0.070						

$(1s\sigma 3d\pi)i^3\Pi_g^-$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	16968.914(17)	4	-0.004	18497.025(19)	5	0.025	19952.756(14)	6	0.034
2	17017.47(2)	5	-0.032	18545.33(2)	9	0.076	20000.436(15)	9	0.124
3	17091.044(17)	5	-0.014	18618.163(16)	8	0.017	20072.116(12)	8	0.054
4	17190.22(2)	5	0.007	18715.65(2)	7	0.074	20167.775(15)	7	0.055
5	17315.208(16)	4	-0.068	18838.130(16)	7	0.020	20287.31(2)	4	0.190
6	17466.29(2)	5	-0.034	18985.45(2)	5	0.024	20430.99(3)	2	0.110
7	17643.211(17)	4	-0.091	19157.50(2)	4	0.010	20598.47(4)	2	0.010
8	17845.71(2)	4	-0.000	19353.99(2)	4	0.030	20789.05(7)	1	0.060
9	18073.46(2)	4	-0.120	19574.38(2)	3	0.010	21002.86(6)	2	-0.500
10	18325.64(3)	3	0.010	19818.25(5)	1	0.040			
11	18601.48(3)	3	-0.140	20084.73(5)	2	0.110			
12	18900.26(4)	3	0.060						
13	19220.93(6)	2	-0.210						
14	19562.52(5)	1	0.080						

**table III.** (Continued.)

$(1s\sigma 3d\pi)i^3\Pi_g^+$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
1	16998.00(2)	4	0.024	18539.50(2)	5	0.040			
2	17086.474(17)	5	-0.014	18617.862(19)	6	0.008	20033.06(2)	5	0.070
3	17202.627(19)	5	-0.007	18725.790(19)	7	0.010	20130.70(3)	3	0.080
4	17343.627(15)	6	-0.047	18860.377(15)	7	0.033	20254.70(3)	5	0.040
5	17508.18(2)	4	-0.026	19019.62(2)	7	0.048	20403.22(4)	3	-0.030
6	17695.856(15)	5	-0.086	19202.388(17)	7	-0.018	20597.14(5)	1	0.050
7	17906.63(2)	4	-0.011	19407.97(2)	6	-0.044	20795.15(5)	1	0.140
8	18140.58(2)	3	-0.110	19635.73(2)	5	0.030	20984.82(5)	1	0.050
9	18397.46(2)	3	0.010				21258.76(6)	1	-
10	18676.88(5)	2	0.000						
11	18978.67(4)	1	0.040						
v = 3				v = 4					
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$			
1	21344.541(12)	2	0.059	22632.03(5)	1	0.030			
2	21408.795(16)	3	0.025	22704.67(5)	1	0.150			
3	21501.76(2)	2	0.096	22791.80(3)	2	0.060			
4	21621.287(18)	3	0.103	22902.73(5)	1	0.010			
5	21765.15(2)	2	0.090	23037.01(4)	1	0.080			
6	21932.05(3)	1	0.060						
7	22120.72(5)	2	0.060						
$(1s\sigma 3d\delta)j^3\Delta_g^-$									
v = 0				v = 1			v = 2		
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
2	17401.30(2)	3	-0.011	18988.127(15)	7	0.023	20511.143(13)	8	-0.003
3	17501.830(13)	5	-0.030	19082.632(11)	9	0.008	20599.883(9)	7	0.047
4	17633.75(2)	3	-0.011	19207.051(15)	8	0.039	20717.119(14)	6	0.091
5	17795.867(14)	4	-0.117	19360.402(16)	6	-0.002	20862.015(15)	5	0.085

**table III.** (Continued.)

$(1s\sigma 3d\delta)j^3\Delta_g^-$									
v = 3			v = 4			v = 5			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
2	21971.433(16)	4	0.087	23370.57(3)	3	0.070	24709.17(5)	2	0.070
3	22054.903(15)	3	0.087	23448.57(3)	3	0.090			
4	22165.210(16)	4	0.080	23551.78(4)	2	0.060			
5	22301.619(15)	2	0.041	23679.34(4)	2	0.030			
6	22463.39(2)	2	0.040	23830.38(4)	2	0.060			
7	22649.128(18)	3	0.032						
8	22858.24(3)	3	-0.020						
9	23089.12(2)	3	0.060						
$(1s\sigma 3d\delta)j^3\Delta_g^+$									
v = 0			v = 1			v = 2			
N	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$	$E_{nvN}$	$n_\nu$	$\Delta E$
2	17401.988(16)	5	-0.028	18988.476(15)	6	0.034			
3	17504.77(2)	4	-0.009	19084.110(17)	6	0.031	20600.596(17)	6	0.084
4	17641.516(16)	4	-0.046	19211.121(14)	6	0.009	20719.229(13)	6	0.051
5	17811.24(2)	4	-0.021	19368.829(19)	5	0.041	20866.399(17)	6	0.051
6	18012.486(19)	4	-0.086	19556.203(17)	4	-0.003	21041.275(15)	6	0.085
7	18243.37(2)	4	0.011	19771.96(2)	3	0.060	21242.90(2)	3	0.135
8	18502.08(2)	3	-0.100	20014.53(2)	2	-0.020	21469.95(2)	3	0.070
9	18786.62(2)	3	0.020	20282.40(6)	2	-0.140	21721.25(4)	2	0.060
10	19095.39(2)	3	-0.130	20573.72(3)	2	-0.010	21963.93(6)	1	0.180
11	19426.70(4)	2	0.070				22251.87(5)	2	0.060
12	19778.99(6)	2	-						
14	20542.39(7)	1	-						
v = 3									
N	$E_{nvN}$	$n_\nu$	$\Delta E$						
3	22054.98(2)	1	0.219						
4	22166.237(14)	2	0.073						